



March 2, 1999

Mr. Frank Anscombe
U.S. Environmental Protection Agency
Region 5 (G-17J)
77 West Jackson Boulevard
Chicago, IL 60604

Mr. Darryl Hogg
Canada Ontario Agreement Coordination
Ministry of Environment
40 St. Clair Avenue West, 12th Floor
Tontro, Ontario M4V 1M2

Dear Darryl and Frank:

The Council of Great Lakes Industries has reviewed the draft report "Great Lakes Binational Toxics Strategy Octachlorostyrene Report: A Review of Potential Sources. We have contacted knowledgeable individuals within most of the industrial sectors discussed in the report. We and the experts whom we have consulted have found the report to be very seriously flawed. This letter, and an extensive report to the OCS Workgroup which, as planned, will follow within the next several days, detail these findings.

Report Approach

The most serious error regarding this second Battelle OCS report (it follows the initial draft OCS Action Plan) is its approach to the assessment of the status of Binational Toxics Strategy (BNTS) challenges regarding OCS. Rather than take an objective view of whether or not the challenges have been met, the report authors seem to go out of their way to deliberately seek the most minuscule, insignificant, and theoretical potential sources. Certainly CGLI expects a rigorous review of source status. But, we expect this review to be conducted on the basis of confirmation of releases through the use of sound analytical techniques. When measurements fail to link a "suspected" source with actual releases, we do not believe it serves any purpose to continue to suggest a "potential" release based on posed theoretical circumstances. Unfortunately, the report does this in several places.

A second serious oversight is the failure to investigate and acknowledge the absence of certain industry sectors within the Great Lakes Basin. The continued use of a particular

technology at a location far removed from the Basin is not, unless special circumstances prevail, likely to have a significant impact on Basin waters. CGLI's sector review work has shown that several suggested sources or processes do not operate within the Basin. We note that a newly released draft Ontario OCS inventory report, although it may suffer from some of the technical shortcomings as the Battelle report, does in fact look first to see if the suggested sources are active in Ontario.

As described below, the most serious technical error is the one-size-fits-all approach taken to apply surrogate measurements and calculate potential OCS releases. As explained in the extensive review produced by Mr. Larry LaFleur of NCASI, comments from whom have also been forwarded by the American Forest and Paper Association, the HCB/OCS or dioxin/OCS relationship for a given source is dependent on many variables and must be carefully determined on a case by case basis. In addition, factors like partition coefficients and other important variables must be considered when extrapolations from sediments are made to predict source releases. Mr. Robert Bailey, a member of the HCB Workgroup, has provided the analysis which appears below.

Sector Analysis

CGLI has undertaken a comprehensive review of the OCS sources in the Battelle report on a sector by sector basis. We have contacted industry experts and solicited comments on the basis for which OCS releases have been suggested within the report. This detailed response is in final preparation stages and will be forwarded to the BNTS OCS Workgroup when completed.

Detailed Technical Comments

As mentioned above, Dr. Larry LaFleur of the National Council of the Paper Industry for Air and Stream Improvement has studied the mechanics of chlorinated phenolic compounds extensively. He has reviewed the second Battelle report and has concluded that from a mechanistic and sound scientific process standpoint, the document is seriously flawed. His observations include the following.

Introduction

A fundamental premise of modern synthetic chemistry is that one needs to understand the basic reaction mechanism before one can reliably predict products. Even if one knows the proper mechanism, the appropriate reaction conditions (e.g., temperature, catalyst, sufficient time, proper solvents, suitable concentrations, etc.) must be present in order for the reaction to proceed. Many reactions which occur in one solvent, such as free radical chlorination in aprotic solvents, would be suppressed in a protic solvent such as water. Finally, the necessary starting materials must not only be present, but must be present in proportions conducive to the reaction. In many respects, synthetic chemistry is the science of successfully optimizing the various combinations of these variables to achieve a specific, desired outcome.

Accordingly, any technically creditable extrapolation from known sources of octachlorostyrene (OCS) to potential other sources requires a careful consideration of reaction mechanisms, conditions, and stoichiometry. Thus, sufficient evidence that each of these criteria have been met must be demonstrated before one would have sufficient cause to further examine a hypothesized new source.

Below, we discuss mechanistic considerations, reaction conditions, and stoichiometry of some known sources of OCS. In this discussion, we highlight the types of corroborating data that would be necessary to extrapolate known OCS sources to other sources. We also give several examples of how a more critical consideration of these fundamental principles would show that there are no data to support the hypothesis that these processes are potential sources of OCS. We briefly discuss the Battelle approach to estimating an OCS inventory based on the EPA dioxin inventory and show that the underlying assumptions are fundamentally flawed.

Mechanistic Considerations

Hexachlorobenzene, octachlorostyrene, and PCDD/F

The Battelle report notes an apparent relationship between hexachlorobenzene and octachlorostyrene where PCDD/F have also been reported. These different mechanisms seem to arise where the starting materials and/or conditions are such that hexachlorobenzene can be formed. Apparently, under these same conditions hexachlorobenzene can further react to form octachlorostyrene or it can proceed through a different series of reactions to form PCDD/F. Under these circumstances, there is an apparent relationship between octachlorostyrene and PCDD/F. However, it would be inappropriate to conclude that the reverse would also be true. If PCDD/F are formed by some other mechanism under other conditions, it may or may not coincidentally produce either hexachlorobenzene or octachlorostyrene. As is discussed in Section V, there are several examples of PCDD/F formation where there is no reason to suspect formation of octachlorostyrene.

The de novo synthesis hypothesis

In the review of sources commissioned by EPA in 1985, Schulman and Klingele¹ discussed theoretical mechanisms for octachlorostyrene formation. They proposed the following hypothesis:

“Each reaction in the stepwise formation of PCSs could fall into one of two broad categories:

1. ultratrace concentrations of reactants combine in high yield; or
2. high concentrations of reactants combine in ultratrace yields

¹ For complete description of references see bibliography contained in Appendix I.

In the former case, the free energy of formation of the product at each step is lower than the free energies of reactants and other competing products. In the latter case, the free energies of formation of reactants and other products are lower than the PCS precursor products, but the statistics of the reaction chemistry assure that some of each of the successive precursor products will be generated in some amounts.

Reaction conditions favoring the former case would probably involve high energy environments where polychlorinated aromatics like PCSs would be stable relative to other molecular configurations. Such conditions would be likely to prevail in high energy electro-, pyro-, photo- and thermochemical reaction environments. Reaction conditions favoring the latter case would involve lower energy reactions in which polychlorinated organic substances are reactants or intended products. Further, if PCSs were removed from the reaction environment faster than other, more stable products, say via physical processes such as sorption to the walls or bottom of a reactor vessel or to particulate matter in the reaction matrix, significant quantities of PCSs could still be generated, even though not thermochemically favored.”

Schulman and Klingele (1985) went on to propose a theoretical mechanism that might lead to the formation of octachlorostyrene through a series of high energy free radical chlorinations and polychloro alkylene radical coupling reactions. This mechanism is termed the *de novo* synthesis mechanism. This mechanism was not proposed based on any experimental investigations on their part, but was instead based on their review of potentially relevant published literature and their interpretations.

Their final conclusions based on their deliberations were:

“Whenever a carbon source is exposed to chlorine and large energy flux, as either electricity or heat, and indicator compounds such as carbon tetrachloride, perchloroethylene, and perchlorobenzene are produced, PCS is a suspected byproduct. Whenever aromatic compounds, particularly chlorinated ones, are exposed to conditions where chloroalkyl radicals may be present, PCS is a suspected byproduct.”

We would add to those observations the fact that the chemistries used to support their hypothesis were free radical reactions occurring under extremely high energy conditions, and were often conducted with a very large excess of chlorine (relative to the available carbon). We believe these are important distinctions.

The Battelle report cites this hypothesis, describes it generally, but does nothing to further advance it or support it with new information.

Based on the rationalizations used to advance this hypothesis, the *de novo* mechanism is clearly a high energy free radical chlorination and coupling mechanism. In order to invoke this mechanism for a potential new source of OCS, one should provide supporting data to

justify the hypothesis. As discussed in the Schulman and Klingele report, one should provide evidence of other intermediates or by-products that support that a similar mechanism is operative. These may include carbon tetrachloride, various tri- and tetrachloro ethanes and ethylenes, hexachlorobutadiene, di-, tri-, tetra-, penta-, and hexachlorobenzenes, etc. Since many of these are actual commercial products, it would be necessary that more than just a single intermediate be identified to support the like mechanism argument.

Magnesium and nickel refining

In one reference, the Battelle report states that there are indications of formation of both OCS and PCDD/F (Oheme et al. 1989) in magnesium and nickel refining. The authors also note that the processes result in the formation of hexachlorobenzene. Oheme et al. describe a unique PCDD/F fingerprint where the PCDF to PCDD ratio is 50:1. This would indicate that it is appropriate to suggest formation of OCS from a source if, and only if, the hexachlorobenzene was demonstrated to be present and the PCDF to PCDD ratio was approximately 50:1. A more detailed examination of the PCDD/F fingerprint reported by Oheme et al. (1989) should be performed, and additional criteria should be considered (e.g., the 1,2,3,7,8-PeCDD to 2,3,7,8-TCDD ratio was 11:1). These criteria would provide a technical justification for assuming a like mechanism might be operative. At the same time, it should also be pointed out that the Oheme et al. work explicitly pointed out the vast differences between the Mg and Ni refining PCDD/F fingerprint and the fingerprint typically observed in incineration sources. This is explicit evidence that there is a completely different mechanism than the one responsible for the OCS from Mg and Ni refining that may be operative in incineration sources.

Other metal refining processes

Doring et al. (1992) describe the concurrent formation of OCS, HCB, pentachlorobenzene (PeCB), decachlorobiphenyl (DCB), and PCDD/F from a copper smelting process. Doring et al. (1992) describe conditions necessary for the formation of these compounds as follows:

“A chlorine source is present (sodium chloride) and the reductive conditions transform Cl⁻ to Cl⁻-radicals. These are then able to chlorinate the aromatics formed by radical processes from the carbon source (coal) at the high process temperature.”

They later note:

“The chlorination roasting process of the copper slag has some similarities with the production of waterfree magnesium chloride (reductive conditions at high temperature (>700°C), presence of carbon and Cl⁻-radicals).”

Much like the fingerprint for the above described Mg process, there is a clear predominance of PCDFs, with the PCDF/PCDD ratio at about 10:1.

This illustrates the importance of corroborating mechanistic hypotheses with confirmatory data. Only when clearly analogous conditions are observed and similar fingerprints are demonstrated (e.g., PCDF/PCDD ratio of 10:1, presence of HCB, DCB, and PeCB) can one reasonably infer the formation of OCS.

Perchloro solvent manufacturing

In the work reported by Pereira et al. (1988), which the Battelle report cites as evidence of a link between OCS and HCB, the authors also report the presence of high levels of di-, tri-, tetra-, and penta-chlorobenzenes, as well as hexachloro-1,3-butadiene and octachloronaphthalene as by-products of chlorinated solvent manufacturing. Thus, before invoking an argument that the presence of HCB is an indication of potential OCS via the same mechanism, evidence of these other co-contaminants that would support the hypothesis of a like formation mechanism should be provided. Otherwise, there is no justification for supposing a like mechanism.

To summarize, before any surrogate chemicals like PCDD/F or HCB can be used as indications of the potential for OCS formation, there should be some corroborative data which provides supporting evidence that a like reaction mechanism is operative. Without such evidence, the extrapolation from one source to others using the presence of these proposed indicator compounds is technically insupportable.

Chlor-alkali production

The Battelle report sites the work of Kaminsky and Hites (1984) as evidence of the formation of OCS in the chlor-alkali process where carbon electrodes are utilized. In work published by Rappe et al. (1990), a PCDD/F fingerprint for this type of process was shown to produce a large predominance of PCDFs. For instance, sludge from electrodes was found to contain 52,000 pg/g 2,3,7,8-TCDF vs. non-detectable levels of 2,3,7,8-TCDD. Similar high ratios were found for the higher homologues. Thus, inferring a relationship between known sources of PCDD/F from electrolytic processes and the potential for production of OCS would only be technically defensible if it were demonstrated that the PCDFs clearly dominated the fingerprint. If another fingerprint is observed, it would be sufficient evidence that an alternative mechanism is operative and that, in the absence of other evidence concerning that mechanism and its by-products, it would be inappropriate to infer the formation of OCS.

Reaction Conditions

Table 1 provides a partial summary of conditions where OCS has been demonstrated to form (as described in the Battelle report, not independently verified). All can be characterized as high energy processes. Some involve high electrical currents, some high temperatures, and some both. In many cases, Cl₂ gas or other chlorinated solvents are used to create certain atmospheres, and conditions are such that they are clearly intended to react. Characterization of other potential sources of OCS should include careful comparison of the conditions known to produce OCS and those of the candidate process.

Table 1. Reaction Conditions of Known Sources of Octachlorostyrene

Process	Temperature	Energy Input	Carbon Source	Chlorine Source
Chlor-alkali	not specified	electric current	carbon electrodes	brine and Cl ₂ produced
Mg refining	1000-1200°C	electrodes	carbon electrodes	Cl ₂ atmosphere
Al degassing	600°C	unspecified, (sufficient to melt Al metal)	hexachloro-ethane	hexachloro-ethane or Cl ₂
Cu smelting	700°C	unspecified, (sufficient to melt Cu metal)	coal	8% NaCl under reducing conditions
Secondary Pb smelting	1260°C	incineration	battery casings	PVC separators

Stoichiometry

Examination of the metals refining processes described in the Battelle report strongly indicates that in most cases there is excess chlorine relative to carbon (high chlorine to carbon ratio). This is also true for the production of carbon tetrachloride and tetrachloroethane. If one considers the chlor-alkali process, where a large volume of Cl₂ is produced from a comparatively small mass of carbon (in the form of the electrodes), there is also a high Cl/C ratio. Under these circumstances, it seems apparent that the potential for the formation of highly chlorinated compounds like OCS exists. However, it would

not be appropriate to assume that if the right temperature and/or other conditions were present, the same potential for formation of OCS exists where the ratio is the opposite.

To a certain extent, dilution may also be an important consideration. Reactions that proceed in high yield at high concentrations may not proceed at all if performed under dilute conditions.

Examples of the Use of These Principles

Pulp bleaching

A perfect example of the need to provide some supportive evidence of like mechanisms is the insupportable extrapolation of the historical presence of PCDD/F in pulp mill effluents and the suggested formation of OCS. It has been well established that the formation of PCDD/F in pulp bleaching was caused by electrophilic aromatic substitution of the unchlorinated dibenzo-p-dioxin and dibenzofuran (Kringstad et al. 1988; Voss et al. 1988; Berry et al. 1989; LaFleur et al. 1990). This type of ionic chemistry occurs because bleaching is performed in an aqueous environment. Free radical chemistry (as invoked by the Schulman and Klingele *de novo* formation hypothesis) is detrimental to the quality of the pulp; thus, steps are taken to suppress this chemistry. In older bleaching processes, this involved the use of 12 to 15% chlorine dioxide, a free radical scavenger. The active chlorinating agent responsible for the formation of PCDD/F in pulp bleaching is Cl₂. In order to eliminate the potential formation of PCDD/F in bleaching, the US and Canadian pulp and paper industry has moved to the use of chlorine dioxide bleaching processes. The switch to this bleaching chemistry has virtually eliminated all TCDD/F formation, and forms the basis of the NPDES effluent guideline limitation recently promulgated by EPA.

EPA conducted extensive sampling and monitoring of a variety of bleaching processes in the development of their effluent guideline (Federal Register 1998; US EPA 1993). This work included testing for many of the compounds that would provide evidence for other potential OCS mechanisms. Included in these analyses were carbon tetrachloride; tri- and tetra-chloro ethanes and ethylenes; di-, tri-, and hexachlorobenzenes; hexachlorobutadiene; and even styrene itself. EPA found no evidence of the presence of these compounds in the bleach plants they studied. This provides further evidence that the types of high energy free radical chemistry required to form OCS are simply not present in pulp bleaching.

To summarize:

The historical formation of PCDD/F in the bleaching process has been demonstrated to be due to an electrophilic aromatic substitution mechanism, not a high energy free radical mechanism.

Since free radical chemistry has undesirable effects on pulp quality, steps are taken to minimize it.

The pulp industry has changed its bleaching practices to the point where TCDD/F formation is virtually eliminated. These process changes have significantly reduced the incidental formation of other chlorinated organics as well.

EPA's data generated during their development of the pulp and paper industry effluent guideline demonstrate the absence of other indicator compounds that should be present if the *de novo* OCS mechanism was operative.

Taken together, there is no justification for extrapolating from the historical presence of PCDD/F in pulp bleaching to the potential for this process to produce OCS. In fact, the clear understanding of the reaction mechanisms responsible for the presence of PCDD/F in historical bleaching processes is evidence that OCS would not be expected.

Vapor phase degreasing

The Battelle report seems to liken the process of vapor phase degreasing with aluminum degassing. In the case of the aluminum degassing process, the temperatures are above the melting point of aluminum (reported by Battelle as 600°C), and either hexachloroethane or chlorine gas are introduced to force their reaction with hydrogen. Comparing this with solid metal parts at or just below the boiling point of the solvent (e.g., 74°C for 1,1,1-trichloroethane) and inferring a potential for the formation of OCS is not technically sound.

Pesticide manufacture

The Battelle report sites pesticide manufacturing as a potential source of OCS. The discussion seems to involve mostly 2,4-dichlorophenol and products made using it as an intermediate. The process cited in the Battelle report is the controlled chlorination of phenol using a reasonably selective chlorination agent. There is nothing in this process that even begins to suggest the kinds of conditions necessary to produce OCS.

The authors state, "The methods for producing 2,4-dichlorophenol include the direct chlorination of phenol and/or monochlorinated phenol using chlorine or sulfuryl chloride (SO₂Cl₂) with chlorination promoters and stabilizers. In as much as this reaction is known to form CDD/CDFs, it is by analogy, suspected of forming OCS," citing Kirk-Othmer 1996. We have examined the Third Edition of the reference (which is the only edition we had ready access to), and find that the statement that "In as much as this reaction is known to produce CDD/CDFs..." is a very misleading interpretation. Kirk-Othmer noted that polychlorophenols are starting materials for the synthesis of PCDDs and use 2,4,5-trichlorophenol as the starting material for 2,3,7,8-TCDD. There is no indication that chlorination is the mechanism responsible. For a discussion of the currently accepted mechanism for PCDD formation in chlorophenol manufacturing, see the following discussion on pentachlorophenol. Other workers (e.g., Firestone et al. 1972) have analyzed technical formulations of dichlorophenolics and found no dioxin contamination.

Pentachlorophenol (PCP) production

Generally, the incidental formation of PCDDs during pentachlorophenol manufacturing is thought to be due to the strong basic conditions and condensation of the chlorophenolate salts with each other (see US EPA 1980 for discussion of reaction mechanism). The initial condensation forms a polychlorodiphenyl ether, which then undergoes an intra-molecular reaction to form polychloro-p-dibenzodioxin. Since technical pentachlorophenol has significant levels of tetrachlorophenols, the PCDD distribution is predominated by OCDD, followed by varying amounts of HpCDD and HxCDD. Generally, PCDFs are at much lower levels. It is also notable that polychlorohydroxydiphenyl ethers are co-contaminants of PCP (Jensen and Renberg 1972; Jensen and Renberg 1973; Nilsson et al. 1974). This fingerprint or product distribution does not resemble any product distribution associated with known sources of OCS. There is no similarity in the reactions responsible for PCDD formation in PCP manufacturing (which are largely ionic) and the *de novo* high energy free radical chlorination and coupling reaction described by Schulman and Klingele (1985). There is no indication that any of the other OCS precursors are present. Thus, no evidence has been presented or is available indicating that there is any similarity to the mechanism for PCDD formation in pentachlorophenol and any known mechanism for OCS formation.

Estimating an OCS Inventory Based on the Presence of PCDD/F

The Battelle report outlines a series of assumptions around ratios of HCB, PCDD/F, and OCS to develop emission factors, then uses the Oheme et al. (1989) sediment data to develop a numerical ratio for extrapolating PCDD/F data to predict or inventory other OCS sources. As was discussed previously, the fingerprint from the metals refining process studied by Oheme et al. (1989) was specifically noted by the authors to be unique. This is actually data that indicate that one should not use this as the basis of a conversion factor for any source other than other metal refining processes, or perhaps the chlor-alkali process, since it clearly demonstrates that this source is unique. Until a link has been established between OCS and a given mechanism of PCDD/F formation, it is totally inappropriate and counterproductive to the goals of the Binational Toxics Strategy to generate “generic” PCDD/F-to-OCS emission factors to estimate source emissions or to develop an OCS inventory. Thus the entire rationale used in Section 4.2 to establish a cornerstone for developing an OCS source inventory is fatally flawed and should be discarded.

Fate Based OCS Release Rate Estimation

Mr. Robert Bailey has reviewed the premise put forth in the second Battelle report regarding the calculation of OCS/HCB/Dioxin ratios from sediments, and their application to suspected source generation rates. He has found this presentation to be seriously flawed. Estimates of OCS releases to the Great Lakes Basin have been grossly over estimated. His comment follow.

As the Battelle authors found when attempting to compile a report on sources of octachlorostyrene (OCS), there is essentially no direct information available on production and releases of OCS. Their approach was to summarize what information they found on the occurrence of OCS in the environment and potential sources. However, there was no segregation of the data by time so that the conclusions are based in large part on older information, reflecting technology and practices from the 1970s and earlier. In addition surrogates were incorrectly used to estimate OCS emissions and concentrations in the environment. **The conclusion that OCS may be currently, 1999, emitted in significant quantity in the Great Lakes region is not supported by the available data.** The reported dramatic decreases in most of the observed concentrations over the past 30 years and concurrent and continuing decreases in related chemicals suggest that OCS may be disappearing from sight in the Great Lakes.

Environmental Concentrations

In the Great Lakes and elsewhere the observation of OCS in the environment has been the clue to production and release of OCS from a variety of industrial processes. Sediment cores in Lake Ontario show a peak in the concentration of many chlorinated chemicals, chlorobenzenes, pesticides and OCS around 1960 (Kaminsky and Hites, 1984, Durham and Oliver, 1983)². Since that time, waste disposal as well as production technology have improved with great reductions in the release of these chemicals to the environment. In fact, already by 1981 Durham and Oliver (1983) reported the concentration of OCS in Lake Ontario sediments had dropped by over 95% from its 1960 concentration. Huestis et al. (1996) report an approximately 90% decrease in the concentrations of both OCS and HCB in fish from Lake Ontario between 1977 and 1993. The concentration of OCS in Niagara River suspended sediments has continued to drop during the period of 1990 through 1995 (Niagara River TMP).

Sources of OCS

The major recent (post-1980) sources of OCS in the environment seem to have been landfills which received waste from the old processes (pre-1980) described in the Battelle report. For example, prior to the 1970s landfill in the Niagara Falls area received “taffy tar” containing OCS and many other chlorinated organics from the production of chlorine. However the release of OCS from these old landfills has been and will continue to be reduced by (a) cleaning old storm sewers of accumulated chemicals and (b) diverting the current landfill leachate from the landfills to wastewater treatment (Niagara River TMP). This storm sewer cleaning and landfill leachate diversion to wastewater treatment has been and is an ongoing part of the cleanup of the Niagara River.

A second example of reduced OCS emissions is the cleanup of the Ashtabula River. Emissions of OCS and other chlorinated chemicals into the Ashtabula River have been

² For complete description of references see bibliography contained in Appendix II

essentially eliminated and a dredging program is planned to remove contaminated sediments which could spread into Lake Erie (Mahan, 1999).

The formation of trace levels of OCS has been documented for a number of processes where chlorine and carbon are present at high temperatures or in electrochemical reactions (Vogelsang, 1986; Kaminsky and Hites, 1984). In general these processes have not been studied closely for OCS because of its low concentrations. As suggested by Schulman and Klingele, it is logical to attempt to predict OCS emissions from the HCB or PCDD/Fs emissions from a variety of processes. The formation of OCS along with HCB, hexachlorobutadiene and polychlorodioxins and furans (PCDD/Fs) from the successive accumulation of two-carbon units, as proposed by Schulman and Klingele, is easy to accept based on the pyrolysis experiments of Lahaniatis (1989). Similarly, the pyrolysis of hexachloroethane used in degassing of molten aluminum in laboratory experiments by Westberg et al. (1997) and qualitatively confirmed by Vogelsang (1986) is consistent with Schulman and Klingele's proposal. However, the formation of PCDD/Fs seems to have a large surface catalysis component which varies widely under different conditions and may be different for OCS. The variations reported in the mixtures of PCDD/Fs from different processes also introduce a great deal of uncertainty in the ratio of OCS production to that of PCDD/Fs. (Summing the different congeners based on their toxicity to calculate a TEQ adds another layer of uncertainty). HCB is chemically more like OCS so that it may be a better surrogate for estimation of OCS concentrations in the environment. However, neither HCB nor TEQ can be considered a good surrogate for OCS in the absence of information linking OCS to each of the wide variety of processes considered in the Battelle report.

In addition, HCB is formed as a byproduct in some specific reactions in the production of highly chlorinated pesticides such as dimethyl tetrachloroterephthalate. Thus, the use of surrogates such as HCB, in the absence of specific information on emission ratios, must be used for only preliminary, order of magnitude, estimates of OCS emissions. Differences in the environmental degradation rates of OCS and surrogates could also change the observed ratio, especially in old samples, and not enough information is available at present to confidently assign the expected change in ratio.

Estimates of OCS emissions from HCB and PCDD/Fs were made in the Battelle report. However, this author will outline below several defects in the Battelle report's estimates of OCS emissions. The first error was taking the relative concentrations of OCS and HCB in sediments as reflecting their water concentrations without correcting for their different partition coefficients. Also, the Battelle report based its ratio of OCS to TEQ (PCDD/F) solely on data from a study of one river, the Elbe. This author proposes using an alternative study based on 400 sites in the U. S. (Kuehl and Butterworth, 1994).

The use of HCB concentrations in environmental samples as a measure of OCS needs to take into account their different physical properties which affect their partitioning in the environment. Neutral chemicals adsorb on sediments in proportion to their octanol/water partition coefficient, Kow (Karickhoff et. al., 1979). The log Kow of OCS is estimated to be

approximately 7.46 from structure activity correlations (SRC online Kow) and the log Kow of HCB, approximately 5.5 (Mackay et. al., 1992). Thus, OCS is estimated to adsorb about 100 times more strongly on sediments than HCB. That is, the concentration of OCS on sediment would be 100 times that of HCB at equal water concentrations.

The OCS/HCB sediment concentration ratio for some sediments are:

Durham and Oliver (1983)	0.15, mean, 1900-1981, Lake Ontario
Oliver and Bourbonniere (1985)	0.11, mean, 1980, 1982, Lakes Huron, Erie
Krieg and Krausch (1993)	0.15, mean, 1985-87, Elbe Estuary
Drouilliard et al. (1996)	0.26, mean, 1996, Detroit River

Thus, the concentration of OCS is estimated to be between 0.01 and 0.001 of that of HCB in the water. Presumably, the relative concentrations of OCS and HCB originally emitted would therefore also be between 0.01 and 0.001.

Atmospheric concentration measurements of OCS and HCB are likely to represent current emission ratios. However, such measurements have not been carried out extensively. Hoff et al. (1992) reported atmospheric measurements of OCS and HCB in 1988-89 in Canada near the shore of Lake Ontario. Unfortunately due to experimental design error, their sampling system did not collect all of the HCB during the summer but still the mean concentrations of HCB were nearly 100 times those of OCS, 54 vs. 0.71 pg/m³. More recent measurements by Dan et al. (1999) did not detect OCS most of the time. HCB is included in the suite of compounds being regularly monitored in the International Atmospheric Deposition Network (IADN) program in the Great Lakes. Results from this program generally show a substantial and steady decline in atmospheric concentrations of HCB and other chlorinated chemicals since 1991 (Cortes et al., 1998, Hillery et al., 1997).

A factor for estimating the environmental concentration of OCS relative to that of 2,3,7,8-TCDD can be derived from the work of Kuehl and Butterworth (1996) in their survey of fish from nearly 400 sites throughout the United States. They report a mean concentration of 2,3,7,8-TCDD in fish of 13.6 pg/g, which made up 55% of the TEQ and a mean of 1.7 ng/g OCS. Converting the mean TCDD concentration to TEQ gives 25 pg/g TEQ which yields an OCS/TEQ ratio of 1700/25 or 68. Correcting for the increased bioaccumulation factor of OCS, 117×10^6 , vs. TCDD, 9×10^6 (Battelle report) suggests a concentration factor of $68/(9/117)$ or OCS = 5.2 TEQ. Using this procedure, the concentration of OCS in the environment, and presumably emissions, would be five times the TEQ concentration. This factor can be compared with the OCS/TEQ factor of 653 used in the Battelle report which was derived from data in the Elbe River. The large number of non-detected OCS concentrations which were included at half the detection limit in the study by Kuehl and Butterworth lead to some uncertainty in the factor of five but this uncertainty is probably less than the overall uncertainty in using such a surrogate for OCS as TEQ.

Larry LaFleur has shown that the one-size-fits-all approach used by Battelle to suggest OCS sources is flawed. Additionally, the errors discussed above in the procedure which they used to establish their ration factors produce erroneous release rate figures. Going

through Table 4 of the Battelle report applying a multiplier of 5 to the dioxin emissions and 0.01 to the HCB emissions yields a different perspective on OCS emissions, about 60 pounds OCS emissions for the entire U. S. versus the 4000 pounds estimated in the Battelle report. Mr. Dan Smith has reviewed OCS levels in the environment and concluded that air deposition is not a significant input vector for the Great Lakes. (See discussion which follows.) Given this finding, out-of-basin sources must be discounted from the 60 pound figure. Once the correct analytical data is used to determine if a source or sector actually releases OCS (or a properly identified and ratioed surrogate), the proper surrogate ratio is identified and applied, the “source” is only included if it is in the Great Lakes Basin, and the continuing operation of the “source” is confirmed, the actual Great Lakes Basin OCS release numbers will be substantially lower, and probably not significant.

The Status and Trends of OCS in the Environment

To confirm the lack of significance of the potential or suggested OCS sources which may remain in the Great Lakes Basin, a review of the status of OCS levels in the environment has been made by Dr. Dan Smith of Conestoga Rovers Consulting. The following analyses reviews his findings regarding the current status and spatial and temporal trends of octachlorostyrene (OCS) in Great Lakes media. These questions were addressed:

- What are current concentrations of OCS in Great Lakes media?
- How have concentrations changed over time?
- How do concentrations vary from place to place?
- What can be deduced concerning current sources and future trends?

Methods: Data on OCS concentrations in Great Lakes media were collected from available sources. Emphasis was placed on analyses of data sets that were extensive and relatively consistent in terms of methods of collection and chemical analyses. While some of the data have been published, most recent data were sought and obtained from various agencies. The Canadian Wildlife Services (CWS) supplied more recent data from that agencies long range monitoring of colonial bird eggs. The Ontario MOE supplied recent data on OCS concentrations spottail shiners from the Niagara River. Unpublished data from MOE’s monitoring of water and suspended solids in the St. Clair and Niagara Rivers were obtained from MOE. The USEPA supplied unpublished data on OCS concentrations in Lake Ontario, collected by the EPA.

Temporal trends were analyzed based on the model of first order decline

$$C_t = C_0 * \exp^{(rt)}$$

Where C_t is the concentration at time t , C_0 is the concentration time 0 or the start, and r is the first-order rate constant. First-order decline assumes that proportional rates of decline are constant over time, that is

$$\frac{dC}{C dt} = \text{constant}$$

First order decline is the most appropriate model for decline of persistent chemicals in the environment because the fate processes that reduce ambient concentrations (e.g., burial, biodegradation, volatilization, photolysis, and dilution) are themselves first order processes. Because temporal trends are assumed to follow first order kinetics, temporal trends were tested with linear regression analysis after transforming concentrations to the natural logs. This produces the following equation

$$\text{Ln}(C_t) = \text{Ln}(C_0) + r * t$$

In which all parameters are the same as in the first equation. The existence of a first order decline can then be tested, statistically, with linear regression of log concentration on time of collection. Logarithmic transformation of concentration also tended to normalize residuals, a requisite for the use of parametric statistics.

Because absolute changes in concentrations fall as concentrations fall, first order reactions will always trace a concave up path when plotted on the usual linear XY graph (Figure 1)³. The inevitable concave up shape, unfortunately, misleads many viewers into believing that concentrations of organochlorines (OCs) are stabilizing over time. Thus, all temporal trends will be depicted on the semilog scale. Time is plotted on the linear X-axis while untransformed concentrations are plotted on a logarithmic Y-axis (Figure 2). Readers unfamiliar with the semilog scale should be advised of the following. First, equal distances on the logarithmic Y-axis represent equal percentage changes in concentration. Consequently first order declines now trace a straight line (Figure 2), eliminating the optical illusion of stabilization that occurs on the linear XY plot. Secondly, absolute changes in concentration tend to look smaller than when plotted on the linear Y-axis, as shown in Figures 1 and 2. When assessing progress over time, therefore, it is important for the reader to look closely at the Y-axis.

Because percent declines per year are more accessible than first-order rate constants, rates of decline over time will be described in the text below in terms of percent declines as opposed to the first order rate constants produced by the regression analyses.

Results

Gull Eggs from the Great Lakes

The CWS eggs sampling program is the best available data base for determining status and trends of organochlorines in the Great Lakes. Since the early 1970s, CWS has assessed OC concentrations in gull eggs from a number of colonies across the Great Lakes. The positions of the colonies are depicted in Figure 3. The gull egg data are extensive over time and space and have benefited from a relatively consistent sampling and analytical methodology (described in Bishop et al. 1992 and Petit et al. 1994)⁴. Another advantage

³ Figures appear in Appendix III.

⁴ For complete reference citations see bibliography in Appendix IV.

of the gull egg data is that the data are regularly disseminated and available to the Great Lakes research community. Thus, the strengths and limitations of these data are better understood than other Great Lakes data sets (e.g., see Smith 1995a, Stow 1995, Hebert et al. 1996, Hebert et al. 1998).

These data were statistically analyzed (by colony and by Great Lake grouping) to determine whether trends were statistically significant. OCS in herring gull eggs declined significantly ($p < 0.05$) from 1987 to 1998 in eggs from all colonies except three – Leslie Spit and Snake Island on Lake Ontario, and Chantry Island on Lake Huron (Figure 4). In the latter three cases, the regressions were marginally significant (e.g, $p < 0.10$). Moreover, when the data from all colonies on a Great Lake were grouped together, rates of decline are highly significant for each Great Lake.

On average, OCS concentrations in gull eggs from colonies on Lakes Erie, Huron, and Ontario tended to be higher than those from Michigan and Superior (Figure 5), although there was considerable variability between colonies on the same Great Lake (Figure 6). OCS concentrations were only sometimes elevated in gull eggs taken from colonies near historical sources such as Channel Shelter Island on Saginaw Bay, the Fighting Island Colony on the Detroit River, and the colonies on Lake Ontario. On the other hand, OCS concentration from the Port Colborne colony on the eastern Basin of Lake Erie and the Niagara River colony were both quite low despite their proximity to historical sources in the Ashtabula and Niagara Rivers (Battelle 1998). The rates of OCS decline over time among lakes were remarkably consistent, despite intralake variability. By colony, rates of decline varied from about 9% per year at Channel Shelter Island to about 24% per year (Figure 7), both on Lake Huron. However, the rates of decline were not significantly different (ANCOVA, $p > 0.05$) across all Great Lakes colonies, and all colonies tended to decline at an average rate of 18% per year. Concentrations of OCS in most colonies are approaching the detection limit (about 1 ppb) (Figures 5 and 6). Eggs were below the limit of detection at least once between 1995 and 1996 in all colonies except two – the Middle Island colony in Lake Erie and the Channel Shelter Island colony in Lake Huron.

Conclusion: From 1987 to 1998, concentrations of OCS in gull eggs fell significantly and somewhat rapidly, on average about 18% per year (Table 3). The rates of decline did not differ statistically among colonies, and declines were very uniform across lakes and connecting channels. These decreases have reduced the concentrations of many colonies to levels near the limit of detection. Spatially, colonies from Lakes Ontario, Erie, and Huron have similar concentrations. Concentrations of OCS in gull eggs from colonies on Lake Superior and Michigan are similar to each other but lower than from the other Lakes.

Spottail Shiners from the Niagara River and Lake Ontario.

Another very useful long-term database for OC in the Great Lakes is provided by spottail shiners represent These data are the property of the OMOE and the Canadian Government, ana collection and analytical methods are described in Suns et al. (1982, 1993) and Suns and Hitchin (1992). As with the gull-egg data, the spottail-shiner data

benefit from relatively consistent methods over the long term as well as frequent sampling over time and space. However, only the data from the Niagara River were obtainable for this report. OCS concentrations in spottail shiners from the upper Niagara River are only rarely above the detection limit, making temporal trends analyses impossible. However, OCS concentrations in shiners from the lower Niagara River were generally above the limit of detection in the beginning of the sampling period in the mid-1980. When less than detect values are assigned the value of $\frac{1}{2}$ the detection limit, OCS concentrations in the lower Niagara River are estimated to have fallen about 8% per year ($p < 0.05$, Figure 7).

Conclusions: Concentrations in shiners taken from the lower Niagara declined at about 8% per year, falling from about 4 ug/kg in the mid 1980s to less than detection in the mid 1990's.

Lake Trout from Lake Ontario

The Canadian Department of Fisheries and Oceans (F&O) collects lake trout and smelt from each of the Great Lakes on an annual basis. F&O data are not readily available to the public or Great Lakes scientific community, so the quality, methods, and extent of these data could not be ascertained. According to information presented in Huestis et al. (1996), lake trout samples from Lake Ontario are analyzed for OCS. These data show significant ($P < 0.05$) declines, about 10% per year, in OCS over time in Lake Ontario lake trout.

Conclusion. Concentrations of OCS fell significantly, about 10% per year, in Lake Ontario lake trout from 1977 to 1993.

Figure 5. Best-fit declines of OCS in herring gull eggs grouped by Lake and Connecting Channel.

Water and Suspended Sediments from the Niagara River

The Upstream/Downstream monitoring group samples water at the beginning and end of the Niagara River, at Fort Erie and Niagara-on-the-Lake. These data, therefore, provide information on water quality conditions in Lake Erie, the Niagara River, as well as information about loading of OCS to Lake Ontario. This is a high quality database with relatively consistent methods over time and very frequent sampling. These data are also regularly published and easily obtainable by the Great Lakes science community.

OCS data were obtained from the Upstream/Downstream sampling group for the period between 1989 and 1995. During this period, water samples were generally taken every week. Whole water samples were divided into aqueous and suspended sediments, and chemical analyses were conducted on these two fractions. Although there are MDLs reported for both fractions -- 0.05 ng/l for the aqueous fraction and 2.7 ng/g of suspended sediment -- concentrations well below the MDL (20% or less of the MDL) are routinely reported. Thus, these reports produce three types of data: estimated concentrations above

the MDL, estimated concentrations below the MDL, and data listed as below the detection limit.

At Fort Erie, at the origin of the Niagara River, 281 aqueous fractions and 285 sediment fractions were analysed⁵. None had a reportable concentration of OCS. Thus, OCS was never detected in 566 analyses representing about 285 water samples. OCS was detected at the mouth of the Niagara River at Niagara-on-the-Lake. For the aqueous fraction, 270 analyses were conducted. Concentrations for the aqueous fraction were 43 times between 1989 and 1991, but not since then. For the adsorbed fraction, reportable concentrations of OCS were detected more frequently concentrations, about 55% of the time. To determine long-term trends, total water concentration of OCS for each sample was estimated in the following manner

$$[\text{OCS}]_{\text{total water}} = [\text{OCS}]_{\text{aqueous}} + [\text{OCS}]_{\text{adsorbed}} * [\text{suspended solids}].$$

Given the large number of analyses below detection, the results of a trends analysis will depend somewhat upon what values are given to unreported values. To insure that trends were real, various values were given to the unreported values for adsorbed OCS: 1/2 the detection limit (1.35 ng/g), 1.0 ng/g, and 0.37 ng/g, the lowest value reported. OCS was rarely reported in the aqueous fraction, so unreported data in the aqueous fraction were set equal to zero.

No matter how non-reported values were treated, OCS concentrations were estimated to have fallen significantly over the period. However, the estimated rate of decrease was dependent upon what values were used for unreported values. OCS concentrations declined by about 40% per year when unreported values were set equal to 0.37 ng/l, but only about 28% per year when unreported values were set equal to 1.35 ng/g, one half the detection limit (Figure 8). Ignoring the aqueous fraction and setting unreported values equal to 1.35 ng/g, OCS concentrations on suspended sediments fell about 21% per year. These analyses demonstrate that OCS concentrations really did decline over this period. However, detecting future declines will become more difficult as more and more analyses yield values below the reporting level.

All of these measured rates of decline are probably faster than the long-term average. Oliver and Charlton measured OCS in the Niagara River several times in the fall of 1982. They found an average OCS concentration of 0.06 ng/l in whole water, which is approximately three times the geometric mean concentrations found in 1989. These two dates trace a 15% per year decline. Similarly, OCS concentrations in the Niagara Bar (discussed below) demonstrate long-term declines of about 14.5% per year.

Conclusion. From 1987 to 1995, OCS concentrations at Fort Erie were always lower than the detection limit in both water and suspended sediments. At Niagara-on-the-Lake

⁵ The number of aqueous data points does not equal the number of suspended sediment data point because data for one or the other medium are sometimes, albeit infrequently, rejected because of QA problems.

at the mouth of the Niagara River, OCS was detected at reportable concentrations on a semi-regular basis, especially adsorbed to suspended sediments. OCS concentrations in whole water and suspended sediments fell rapidly over this period, between 21% to 40% per year, depending upon the value applied to unreported values. Based on these data, loading of OCS to Lake Ontario is estimated to have decreased about 70% or more between 1989 and 1995.

Suspended sediments and water from the St. Clair River

MOE monitors water at two points in the St. Clair River, Port Edward at the beginning of the of the St. Clair River and downstream at Port Lambton. The methods are similar to those used in the Upstream/Downstream sampling: sampling on a frequent basis (every two to three weeks), fractionation into an aqueous and sediment fraction, detection limits of 0.05 ng/l and 2.7 ng/g, respectively, and analysts who routinely report concentrations below the detection limit. Of 103 analyses of the aqueous fraction sampled at Port Edward between 1987 and 1996, only 5 samples had reportable concentrations of OCS. These 5 samples averaged 0.02 ng/l OCS. Only two of 111 analyses of suspended sediments had reportable concentrations of OCS.

Reportable concentrations were more frequent downstream at Port Lambton. Of 141 analyses of the aqueous fraction taken between 1987 and 1994, only 7 had reportable concentrations of OCS. However, OCS was regularly reported adsorbed to particles. About 90% of analyses of suspended sediment yielded reportable concentrations of OCS (Figure 9). When unreported concentrations are set equal to one half the detection limit, these data produce a significant decline of about 15% per year.

Conclusions: OCS concentrations have generally been well below the limit of detection at Port Edward at the origin of the St. Clair River. Downstream at Port Lambton, OCS concentrations dissolved in water are also infrequently detected above the detection limit. However, concentrations adsorbed to suspended sediments are generally at reportable concentrations, although these concentrations appear to be falling at about 15% per year over the last decade.

Data for the St. Lawrence River/Outflow from the Lake Ontario

Environment Canada also samples OCS at the origin of the St. Lawrence River. These data are diagnostic of St. Lawrence conditions as well as Lake Ontario. The data are apparently generated using the same general methods as with Niagara River and St. Clair River sampling. Reported detection limits were 0.07 ng/l for water and 2.7 ng/g for the adsorbed fraction. For 85 samples taken from 1989 to 1994, OCS concentrations were reported once in the water column and 11 times in the suspended sediment fraction. All of the reported concentrations were below the detection limits. The eleven concentrations reported for the sediment fraction 0.9 ng/g. The single value reported for the aqueous fraction was 0.01 ng/l, which is 1/7th the MDL.

Conclusion. Concentrations of OCS in the headwaters of the St. Lawrence River/outflow of Lake Ontario are infrequently detected at concentrations that can be estimated. Current concentrations are well below the detection limit.

Bottom Sediments from Lake Ontario

Two sediment core samples have been taken from Lake Ontario and analyzed for OCS. Durham and Oliver (1983) took a sediment core in the Niagara Bar in 1981, and core samples from the Niagara Bar were taken in 1995 by New York Department of Environmental Conservation (NYDEC 1996). The two cores showed a consistent pattern (Figure 9). In both cores, OCS concentrations in sediments apparently peaked about 1960 and then declined at about 13.5%.per year (Figure 10). For the NYDEC sample, OCS concentrations in sediments deposited after about 1981 were always below the detection limit, which ranged from about 13 to 6.4 ug/kg.

The yearly declines estimated between 1960 and 1981, when OCS concentrations were above the detection limit, can be extrapolated to the present. Assuming that past rates of decline continued to the present, OCS concentrations in Niagara Bay sediments in the early 1990s should be between 0.5 and 1.0 ug/kg (Figure 8). This projection can be compared to the sediment trap data from the Niagara Bar (Oliver and Charlton 1988) and suspended sediment data from the Upstream Downstream Monitoring of the Niagara River (see section above on the Water Concentrations in the Niagara River). Sediments captured in sediment traps should reflect sediments being laid down during that period. Similarly, OCS concentrations in sediments deposited in the Niagara Bar should be a function of OCS concentrations on suspended sediments at the mouth of the Niagara River, which is the source of most particles settling onto the Niagara Bar.

In both cases, however, concentrations of settling and suspended sediment must be normalized to organic carbon levels similar to those found in bottom sediments to reflect the reduced binding capacity of coarser, less organic sediments that finally settle onto the Niagara Bar. Most recently deposited Niagara Bar sediments are about 3.1% organic carbon (NYDEC 1996). Organic carbon concentrations found in sediment traps were about twice those found in settled sediments (Oliver and Charlton 1988). Thus, sediment trap concentrations were divided by two to normalize for organic carbon (Figure 10). The concentrations measured by Oliver and Charlton fall very near the extrapolation line.

The fraction of organic carbon in Niagara River suspended sediments varies considerably, ranging between about 5% to over 30% organic carbon (Kuntz 1988)⁶. Assuming a geometric mean concentration of 10% would require a correction factor of 3.2 to normalize the suspended sediment to the 3.1% organic carbon of the deposited sediments. When concentrations of OCS on suspended sediments from the mouth of the Niagara River are divided by this correction factor, most recent suspended sediment concentrations

⁶ These data were kindly supplied by J. Merriman, Ecosystem Health Division of the MOE.

also fit right on the extrapolation line (Figure 10). This combination of information suggests that OCS loading to Lake Ontario has continued to fall at about the same rate (about 14.5% per year) from 1960 to the present.

Conclusion: As evidenced by OCS concentrations in Niagara Bar sediments, loading of OCS to Lake Ontario apparently peaked in the early 1960s, and has fallen about 14.5 % per year since that time to the early 1980s, when concentrations became too low to be detected. More recent data on settling particles in the Niagara Bar region and suspended sediments in the Niagara River have concentrations similar to those extrapolated from the long-term trends, suggesting that this rate of decline has continued to the present.

Additional Data on Status and Trends. OCS was measured in Lake Ontario water column twice, in 1984 (Oliver and Niimi 1988) and 1996 (EPA, unpublished data). Both samples were taken during spring overturn in open water areas of the Lake and were replicated at several sampling locations. Oliver and Niimi report a mean OCS concentration of 4.7 pg/l in the aqueous phase. For the 1996 EPA sampling, all samples yielded concentrations below the detection limit: roughly 0.5 pg/l in the aqueous phase and 0.2 pg/l in the adsorbed phase. As OCS was not detected in any of the 4 samples (three stations with one station duplicated), it can be assumed that the real OCS concentration was well below the detection limit. A reasonable assumption is that the concentration was $\frac{1}{2}$ the detection limits, or about 0.25 pg/l. Using these two dates only, there was about a 95% decrease in water column concentrations of OCS, or about 22% per year. This observation should be treated with caution. Only two periods were sampled, and the analyses were conducted by different analysts.

Discussion.

The above analysis was limited to straightforward description of observable status and trends of OCS in Great Lakes media. These analyses addressed basic questions of how OCS concentrations have varied in time and space. In the context of the “virtual elimination strategy”, there is also the less straightforward question of what spatial and temporal trends really mean. Specifically, can spatial and temporal trends in measured concentrations be used as an indicator of underlying trends in external loading?

The simple answer to this question is “no.” The problem with inferring changes in loading from changes in ambient concentrations is twofold. First, measured concentrations in many media are often not good indicators of in-lake inventories, especially when measurements are limited. Second, for systems at non-steady-state with external loading, trends of in-lake inventories may be based largely upon internal fate processes and have little or nothing to do with trends in external loading (Endicott et al. 1992a,b, Smith , under review.) With respect to the first problem, concentrations of organochlorines in biota (lake trout, gull eggs, spottail shiners) are known to respond to a number of other factors in addition to abiotic concentrations and levels of external loading. These factors, which confound interpretation of observed trends, include winter weather, prey availability, aquatic prey chain length and structure, terrestrial vs. aquatic foraging,

limnological factors, and potential effects of inter-lake migration (Rasmussen et al. 1990, Rowan and Rasmussen 1992,; Smith 1995a,b, under review; Hebert et al. 1995; 1998) Concentrations of chemicals in the water column and sediments are confounded by sampling error and actual variability due to storms and mixing events as well as long-term changes in lake trophy and suspended sediments concentrations.

In view of the confounding factors affecting organochlorine concentrations, caution should be exercised when extrapolating observed trends, over time and space, in any of the media above to underlying trends in in-lake inventories, and from there, to trends in external loading. This is especially true of inferences based on small data sets and short time trends. For example, consider the OCS data for gull eggs from Lake Ontario (Figure 11). The long-term trend from 1987 to 1998, which shows a significant decrease in OCS concentrations over time, actually consists of three short-term trends: concentrations tended to remain constant from 1987 to 1993, fell precipitously, about 90%, from 1993 to 1995, and then rebounded somewhat from 1995 to 1998 (Figure 11).

Several factors suggest that none of these short term trends is responding to underlying changes of in-lake inventories levels or external loading of OCS. For example, the initial period of stable concentration is more likely attributable to one of the confounding factors affecting organochlorine concentrations in gull eggs (e.g., food chain effects and/or the weather effect). This is apparent because most of the organochlorines also show stable concentrations from the period 1987 to 1993 (Smith 1995a). The organochlorines have disparate sources of external loading to Lake Ontario, and it is not reasonable to expect that the loading of the different external sources of different organochlorines would be synchronized. The short-term pattern of stable OCS concentrations in gull eggs is also inconsistent with data from Niagara River loading. The Niagara River should be the primary external source of OCS to Lake Ontario. Loading of OCS from the Niagara River declined rapidly, from 70 to 80% at the same time that gull egg concentrations remained constant (Figure 8 vs. Figure 11). With respect to the precipitous decline of OCS concentrations from 93 to 95, it is highly unlikely for OCS inventories in Lake Ontario to fall much more than 10% per year, even under condition of complete zero loading (e.g., see Endicott et al. 1992a).

On the other hand, more reliable indicators of trends in ecosystem inventories, but not necessarily external loading, can be obtained by focussing on long-term trends and by looking for similar trends among different media. Despite potential problems with any one data set, there is a high degree of certainty that OCS concentrations have really been falling over the period from 1980 to at least the mid-1990s in Lake Ontario. As summarized in Table 3, there are statistically significant and quantitatively substantial declines in all of the following media:

- inflowing Niagara River water concentrations (1989 to 1994)
- spottail shiners residing in that inflowing water
- in-lake water column concentrations (1994 to 1996, two dates only)
- gull eggs (1987 to 1998)

lake trout (1977-1993)
in-lake sediments (1960 to 1981 or 1994 if suspended sediment data can be included).

Similarly, we can be reasonably certain that OCS concentrations in the St. Clair River/Detroit River are also actually declining, because OCS concentrations are declining in the water column, gull eggs. Data on temporal trends in other Great Lakes areas are mostly limited to gull eggs. This might be problematic, except that OCS levels are falling at all of these other colonies, suggesting that OCS inventories are indeed declining in the Great Lakes. Equally important, Lake Ontario and the St. Clair/Detroit River are two of the three areas in which OCS levels are elevated. With the exception of Saginaw Bay, where OCS is also elevated in gull eggs, temporal trends in other Great Lakes areas are of less importance because levels in most media are already near or at the detection limit.

Keeping in mind the limitations of the data, the following addresses the questions posed at the beginning of this discussion.

- **What are current levels of OCS in Great Lakes media?**

As shown in Table 2, current levels of OCS in most media are now at the limit of detection or rapidly approaching this limit at most sites in the Great Lakes. The notable exceptions to this are OCS concentrations in lake trout in Lake Ontario. Extrapolating past rates of decline (about 10% per year) onto early 1990's concentrations (about 30 ug/kg in whole raw lake trout) suggest that whole raw lake trout will continue to exceed the current detection limit (1ppb) till about 2025. It is also likely that OCS is above the detection limit in fish from the other Great Lakes, and potentially the St. Clair/Detroit River and Niagara River. Assuming a relatively constant relationship between gull eggs and fish, it is likely that OCS would be about as high in Lake Erie and Lake Huron fish as in Lake Ontario. OCS might also be detectable in very large lake trout from Lake Superior and Lake Michigan.

- **How have levels changed over time?**

In all media with adequate data, levels of OCS are decreasing significantly and, compared to other organochlorines, relatively rapidly, e.g., 8% to 30% per year (Table 3). Rates of decrease over time are generally highly statistically significant, quantitatively substantial, and consistent across media, time, and space. It can be concluded with a high degree of certainty that OCS concentrations in the Great Lakes have declined dramatically over the last two decades.

- **How do concentrations vary over space, i.e., from place to place?**

Gull egg data suggest that OCS burdens in Lake Huron, Lake Erie, and Lake Ontario are higher than in Lakes Superior and Michigan, although there is substantial intra-lake variability between colonies from Lake Erie and Huron. Elevated concentrations appear

to be related to historical sources in Saginaw Bay, the St. Clair River, and Lake Ontario. Data from other media are limited, but tend to support the spatial trends found in gull eggs.

- **What can be deduced concerning current sources and future trends?**

The available data suggest that atmospheric sources were probably never an important source of OCS to Great Lakes ecosystems. Gull eggs colonies with elevated concentrations are generally downstream of historical sources of OCS in Saginaw Bay, the St. Clair River, and the Niagara River. Concentrations of OCS in gull eggs from colonies on Lake Michigan and Lake Superior, which are far away from historical sources, tend to be about about 3 to 4 times lower than those downstream of suspected historical sources. It is also important to note that concentrations of OCS in gull eggs from all of the colonies are fallin at about the same rate in all Lake groupings (Figure 5). This observation is inconsistent with the hypothesis of significant current atmospheric inputs, as one would expect atmospheric dependent sites to decline at a different rate than colonies primarily affected by past and current riverine and point sources. The rapid decreases in OCS concentration in gull eggs and the other media also suggest that current atmospheric loading is relatively insignificant and allows unimpeded declines of OCS in the lakes. Consistent with all of these observations, OCS is rarely if ever detected in air monitoring near the Great Lakes (Dann 1997).

If atmospheric loading of OCS can be assumed to be negligible, that leaves current external loading from point and non-point sources and internal loading from sediment inventories of past external loading. It is critical to differentiate between internal and external loading. External sources are generally controllable and likely to yield some benefits if controlled. Sediment inventories, on the other hand, are not readily easily controlled and will remediate naturally without further action.

The two different sources should produce different patterns over time and space. Systems whose OCS concentrations are tightly controlled by external sources should have very site specific and unique temporal patterns, because external source control will be a site-specific function of regulatory commitment, local economic conditions, amenability to control, and other site specific factors. Thus, if, as is often hypothesized, sites on the Niagara River are a major current source of OCS to the Lake Ontario, one would expect declines in OCS in the Niagara River and Lake Ontario media to be episodic, tied tightly to specific remediation activity. It is also expected that the temporal patterns of decline will be very different from OCS declines at other sites, and very different from declines of other chemicals with similar fate processes (e.g. PCBs and DDE) not associated with sources of OCS.

The patterns of decline for systems controlled by internal sediment stores are likely to be very different. As the fate processes controlling declines in sediments are relatively constant across time and space and across PTS chemicals, one would expect systems controlled by internal inventories to decline at fairly similar rates through time, and across

lakes and across PTS chemicals. The data, while limited, seem more consistent with the latter hypothesis. The very similar declines of OCS in the gull eggs across colonies suggests some common mechanism of decline (e.g, fate processes affecting sediment inventories.)

Great Lakes system dominated by internal sediment inventories should also have orderly declines of different persistent toxic substance. That is, concentrations of different organochlorines should decline in a predictable fashion based on the vulnerability to fate processes affecting concentrations in the sediments. More volatile and degradable chemicals like hexachlorobenzene should dissipate faster from the Great Lakes than more stable, less volatile chemicals such as Mirex and dieldrin. PCBs are of intermediate vulnerability and should dissipate with an intermediate speed. The predicted rates of relative decline for internal inventories of various organochlorine can be estimated from the model of Endicott et al. (1992a) under a condition in which external loading was reduced to zero. In this case, long-term declines of these chemicals depends on vulnerability to various loss processes. These estimated zero-loading declines can be compared to yearly declines observed for lake trout in Lake Ontario (Huestis et al. 1986). As can be seen from Figure 12, there is a significant relationship between predicted and observed declines of different organochlorines (regression analysis, $p < 0.05$). That is, as predicted, the different organochlorine are declining in a significantly orderly process, further supporting the hypothesis that external loading is unimportant. It is also important to note that OCS is actually declining faster than predicted. At the least, this graph demonstrates that OCS, which has received little regulatory attention in the last several decades is declining considerably faster than compounds like DDT, PCBs, and TCDD, which have been under very strict regulation. This observation is inconsistent with a system dominated by external sources, which ought to be more controllable.

There are other data to substantiate that current concentrations of OCS in Lake Ontario are based on internal sediment inventories as opposed to current external loading. Loading from the Niagara River can be estimated from the Upstream/Downstream monitoring. Best estimates of early 1990s loading from the Niagara River are about 4.3 to 6 grams per day, depending upon what values are assigned to non-detection data. According to Endicott et al, model, this loading of OCS should produce lake trout concentrations of about 5.2 to 3.8 ug/kg in whole lake trout. These predicted values are 6 to 8 times lower than observed concentrations for this period, about 31 ug/kg (Huestis et al. 1996). The discrepancy between observed and predicted concentrations also supports the hypothesis that OCS concentrations in Lake Ontario are largely due to internal sediment inventories, as opposed to current external loading.

Table 2. Summary of results. Decreases are based on regression analyses. ND means not detected.

Medium	Location	Time Frame	Decrease (% per year)	Most recent conc.
Gull egg	Lake Ontario	1987-1998	Yes (17%)	Some ND
Gull egg	Lake Erie	1987-1998	Yes (16%)	Some ND
Gull egg	Lake Huron	1987-1998	Yes (16%)	Some ND
Gull egg	Lake Superior	1987-1998	Yes (17%)	Some ND
Gull egg	Lake Michigan	1987-1998	Yes (20%)	Some ND
Gull egg	Niagara River	1987-1998	Yes (17%)	Some ND
Gull egg	Detroit River	1987-1998	Yes (20%)	Some ND
Spottail Shiner	Lower Niagara River	1985 -1995	Yes (8%)	100% ND
Spottail Shiner	Lake Ontario	1985 -1995	NA	100% ND
Lake Trout	Lake Ontario	1977-1993	Yes (10%)	0 % ND
Water	Niagara River	1989-1995	Yes (16%-21%)	50% ND
Water	Upper Niagara River	1989-1994	NA	100% ND
Water	Lake Ontario	1984, 1996	Yes (20%)	100% ND
Water	St. Clair River (Port Edward)	1989-1996	Yes (15%)	>95% ND
Water	St. Clair River (Port Lambton)	1989-1995	NA	10% ND
Water	St. Lawrence	1989-1996	NA	90% ND
Sediments	Lake Ontario	1960-1981 (95)	Yes (12%)	100% ND

CGLI appreciates the opportunity to provide these comments. We look forward to working with the Workgroup to correct the process and technical errors represented by the Battelle report.

Sincerely,

George H. Kuper, President
and CEO

Appendix I

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Appendix II

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Appendix III

Figures 1 - 12

Status and Trends of OCS In Great Lakes Media

Figure 1. First order decline (10% per year decrease) on linear XY plot

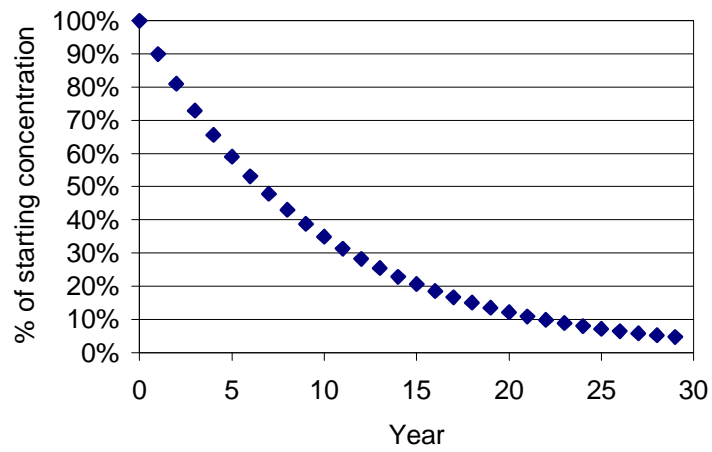


Figure 1. A first order decline graphed on the more usual linear XY plot.

Figure 2. First order decline (10% per year decrease) on semi-log XY plot

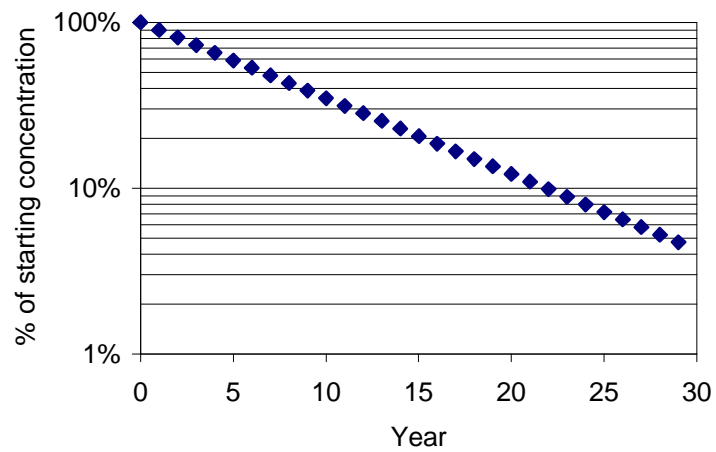


Figure 2. The same first order decline plotted on semi-log paper.

Figure 3. Location of Herring Gull colonies on the Great Lakes.

Figure 4. Yearly % Decline vs. Colony

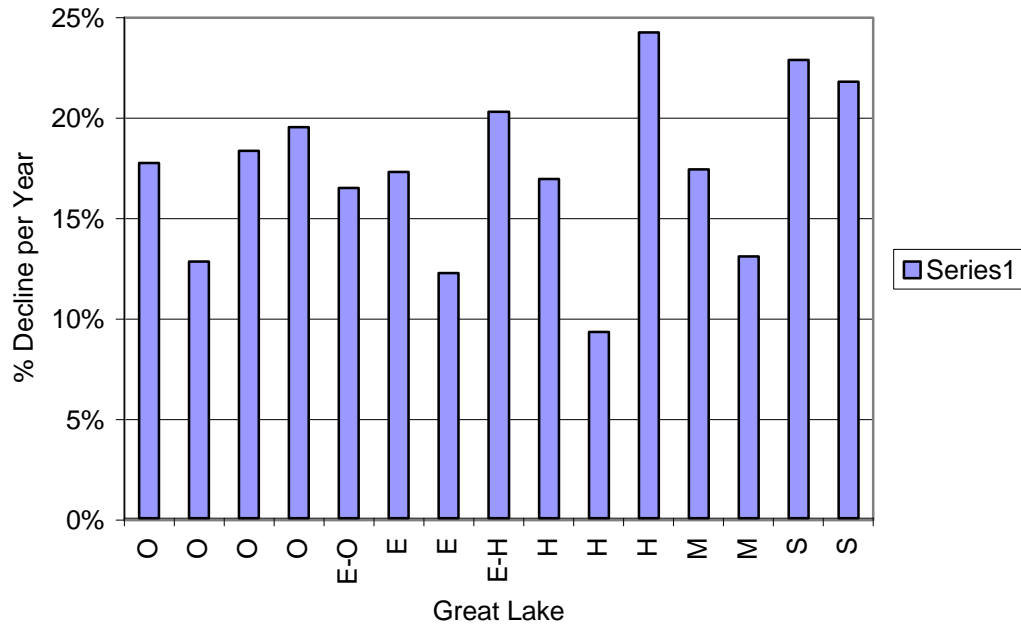


Figure 4. Best-fit % declines per year estimated from linear regression. Colonies are plotted in the following order which generally follow an east-west gradient: Lake Ontario colonies in the order of Strachan Island, Snake Island, Leslie Spit, Hamilton Harbor, Niagara River, Lake Erie colonies in the order of Port Colborne and Middle Island, Detroit River, Lake Huron colonies in the order of Channel Shelter Island, Chantry Island, and Double Island, Lake Michigan colonies with ?/ and ??, and Lake Superior colonies Agawa Rock and Granite Island.

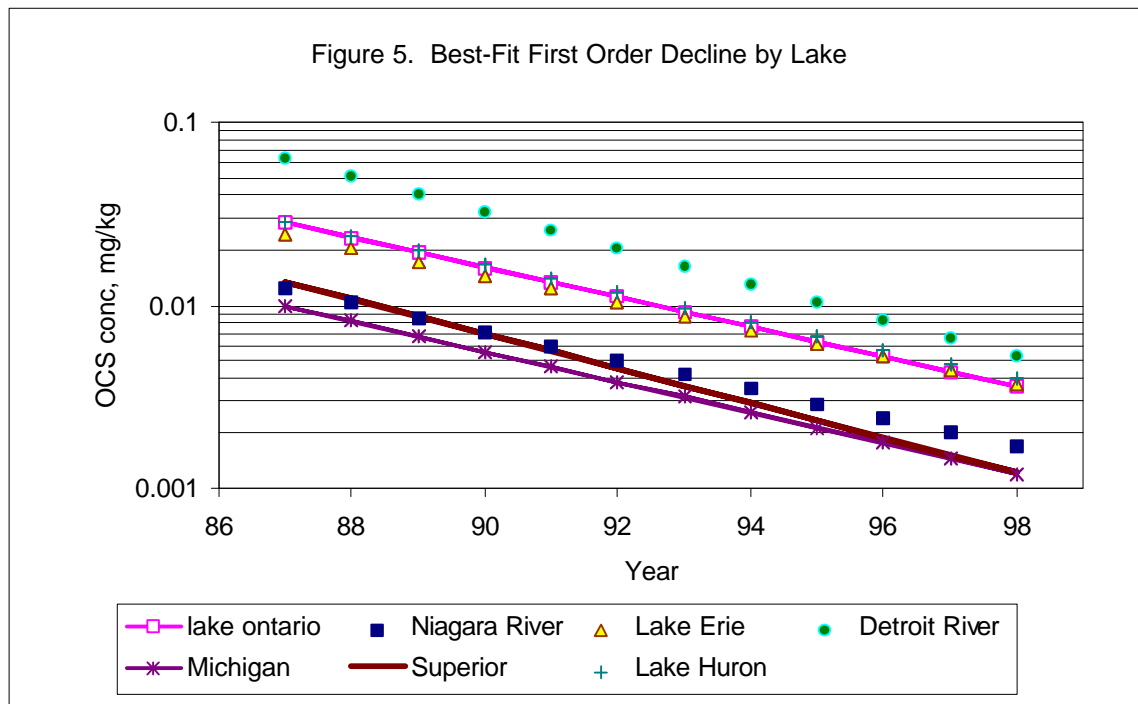


Figure 5. Best-fit declines of OCS in herring gull eggs grouped by Lake and Connecting Channel.

Figure 6. Mean OCS (94-98) versus Lake

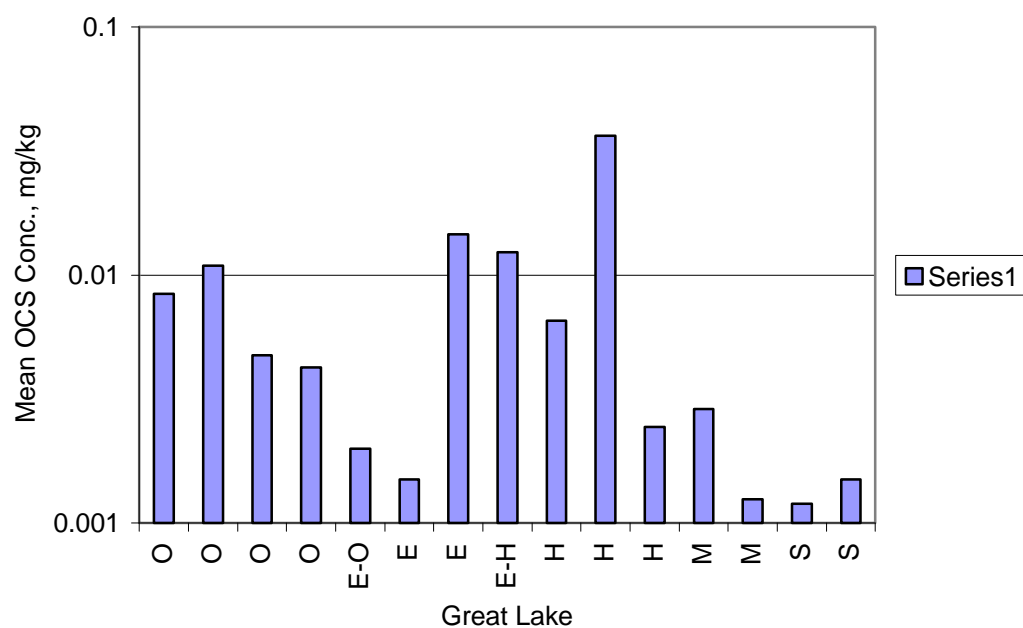


Figure 6. Most-recent (1994 to 1998) concentrations of OCS by colony. Sequence of colonies same as in Figure 6.

Figure 7. OCS in Spottail Shiners in Lower Niagara River (MOE Data)

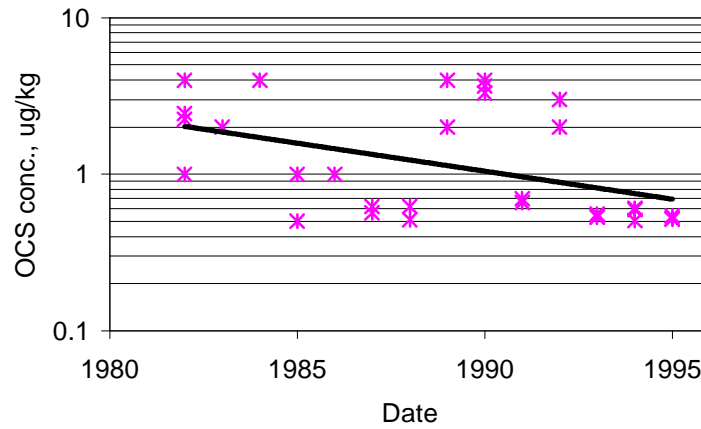


Figure 7. OCS concentrations in spottail shiners from the lower Niagara River. Values less than detection limit (1 ug/kg) set equal to 0.5 ug/kg. Some data points have been altered somewhat (e.g., 10% to 20%) to aid viewing when more than one sample on the same date had the same concentration.

Figure 8. Estimated whole water concentrations of OCS at
Niagara-on-the-Lake

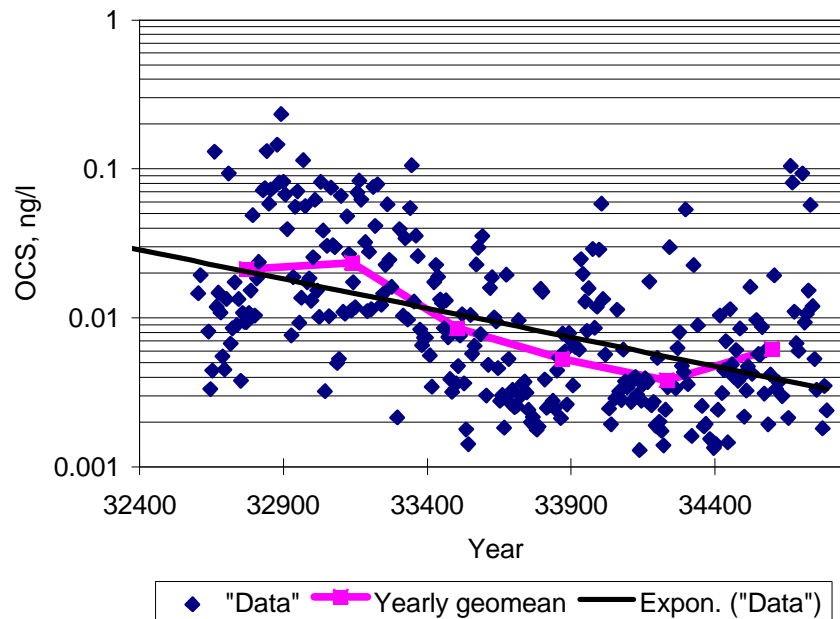


Figure 8. Concentrations of OCS in Niagara River water at the mouth of the Niagara River.

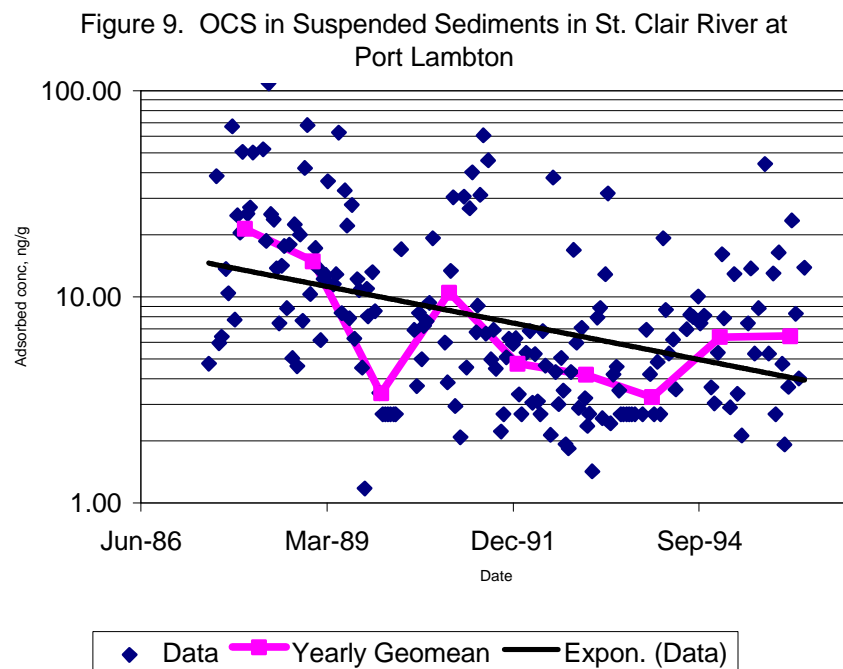


Figure 9. Concentrations of OCS on suspended particle from the St. Clair River at Port Lambton.

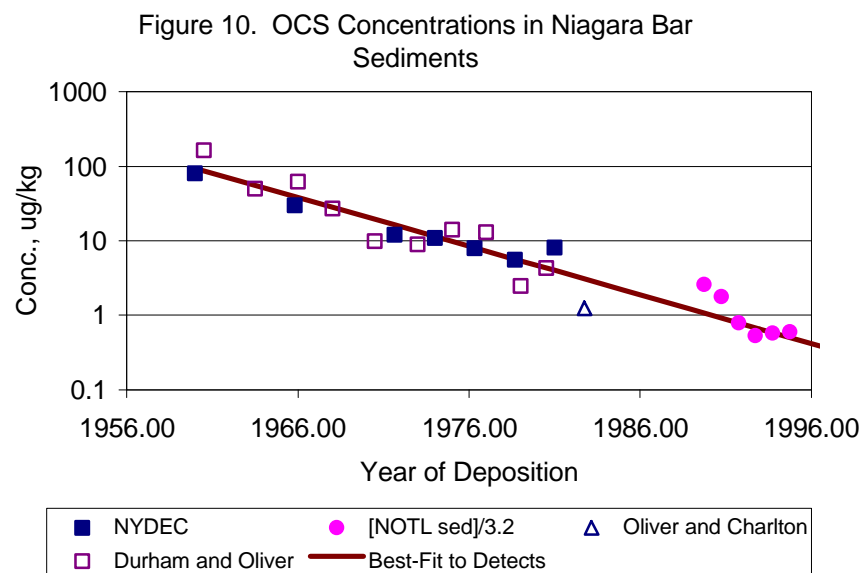


Figure 10. Concentrations of OCS in sediments from Lake Ontario. For the NYDEC sample, all analyses for sediments deposited between 1981 and 1995 were below the detection limit, but these data are not depicted on this graph.

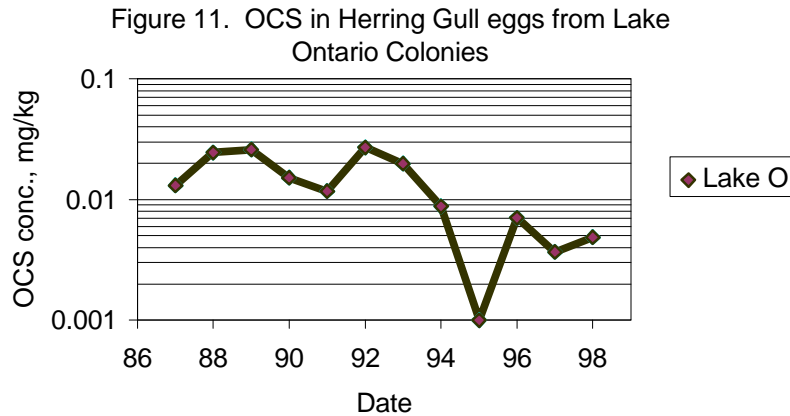


Figure 11. Mean concentrations of OCS in gull eggs from the four Lake Ontario gull egg colonies (Strachan Island, Snake Island, Leslie Spit, and Hamilton Harbor.)

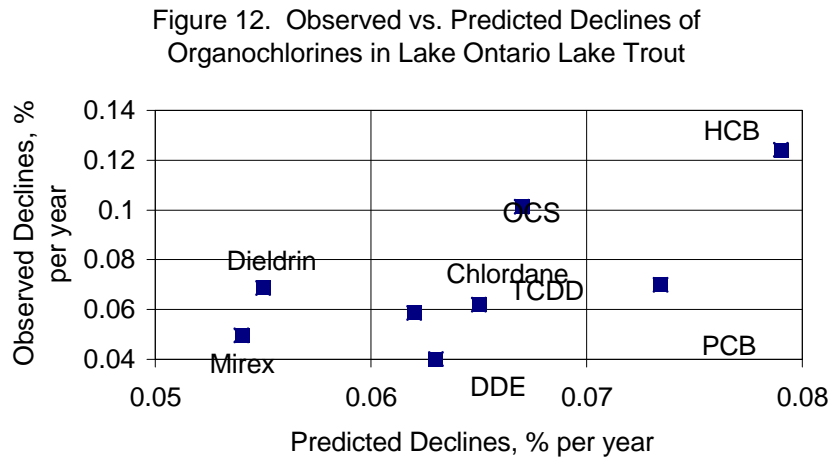


Figure 12. Observed versus predicted declines of different organochlorines in Lake Ontario lake trout. Predicted rates of decline (per year) from the Endicott et al. model (1992a) after cessation of loading. Observed rates are best-fit declines observed in lake trout, data from Huestis et al. (1996).

Appendix IV

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Status and Trends of OCS in Great Lakes Media

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March 1, 1999

Mr. Frank Anscombe
U.S. Environmental Protection Agency
Region 5 (G-17J)
77 West Jackson Boulevard
Chicago, IL 60604

Mr. Darryl Hogg
Canada Ontario Agreement Coordination
Ministry of Environment
40 St. Clair Avenue West, 12th Floor
Toronto, Ontario M4V 1M2

Dear Darryl and Frank:

The Council of Great Lakes Industries (CGLI) is pleased to submit our report regarding octachlorostyrene (OCS) releases, to the Great Lakes Binational Toxics Strategy (BNTS) OCS Workgroup. It represents the combined efforts, and extremely hard work, of many. It addresses suggested industrial sources of OCS on a sector-by-sector basis, provides a review of OCS levels in the environment, discusses OCS formation mechanisms, assesses the environmental fate of the substance, and evaluates the use of HCB and dioxin surrogates for estimating OCS release inventories.

Much of the sector-by-sector information has been provided by industry contacts. Many of these contacts have submitted some or all of this information separately to either U.S. EPA Region 5 or Environment Canada. Others have chosen to funnel their information through CGLI via this report. Our agreement with information providers has been that we will forward the information which they provide, to the governments on an anonymous basis. For that reason, the sector review section of this report contains few references. CGLI will gladly direct any questions which the governments or Workgroup members may have back to the appropriate parties to facilitate discussion on the few issues which may remain.

The OCS environmental status section is an extremely important and telling portion of this report. It shows that this material is disappearing from the Lakes at very high rates, faster than any other organochlorine. This decay rate (8 to 30% per year) demonstrates that any remaining OCS sources are insignificant. This work also highlights the importance of

Location: 3600 Green Court, Suite 710
ANN ARBOR, MI 48105
USA

Mail: P.O. Box 134006
ANN ARBOR, MI 48113
USA

Tel: 734-663-1944
Fax: 734-663-2424
Web: www.cgli.org

environmental fate and mass balance assessments as a means for assessing virtual elimination progress for priority chemical substances.

The report examines the practice of using surrogate relationships (HCB and dioxin releases) to estimate OCS release rates when source specific OCS data is not available. The conclusions are that these relationships are very process specific and should not be used unless the exact case-by-case ratio is known or determined experimentally.

It is notable that the OCS release elimination or reduction progress reported in the sector-by-sector review section was accomplished through a range of measures. Some processes have been shutdown, some modified, and others outfitted with additional or enhanced treatment technologies. This success demonstrates the multi-pathway options which are available and can produce virtual elimination outcomes.

Finally, the comprehensive nature of this report reflects the special circumstances regarding OCS, relative to other Level I substances on the BNTS list. Little source information regarding OCS is in common circulation. Industry personnel, prior to the CGLI information request effort, had not looked closely at the release of this specific substance. Because OCS has not been a “main stream” substance in regulatory circles, because the material is disappearing rapidly from the Great Lakes ecosystem, and in light of the attempts which have been made by the Battelle OCS report and newly drafted Canadian OCS inventory document to estimate releases on the basis of surrogates, a special effort was needed provide the proper perspective regarding this material.

We look forward to continuing our work towards successful implementation of the BNTS and would be pleased to answer questions regarding this report. You may direct them to me, Werner Braun (703) 741-5815 (werner_braun@cmahq.com), or Dale Phenicie (770) 487-7585 (dkphenicie@mindspring.com).

Sincerely,

George H. Kuper, President
and CEO

cc: Gary Gulezian
Liz LaPlante
Ron Shimizu
Alan Waffle

**Octachlorostyrene
and
Suggested Industrial Sources**

**A report to the
Great Lakes Binational Toxics Strategy
OCS Workgroup**

March 9, 1999

**Council of Great Lakes Industries
3600 Green Court, Suite 710
Ann Arbor, MI 48105**

Acknowledgments

This report was produced by the Council of Great Lakes Industries (CGLI), through the greatly appreciated hard work of many people in industry who voluntarily provided their time and effort toward the success of the Binational Toxics Strategy. The information contained, regarding octachlorostyrene (OCS) releases to the Great Lakes, was acquired through a multi-Industry/multi-company participative effort requiring hundreds of conversations, meetings with many industrial groups and organizations, and responses to information requests and questionnaires.

The report was prepared by Dale K. Phenicie (Environmental Affairs Consulting), with assistance from Werner Braun (V.P. of CGLI and U.S. co-chair of the CGLI OCS Working Group), Don Hames (Dow Canada and Canadian co-chair of the CGLI OCS Working Group), Bob Redhead (Robert J. Redhead Ltd.), with contributions from representatives of CGLI member companies, many others within industry, and representatives from U.S. and Canadian industry trade associations. These efforts have provided the important picture regarding industrial process use and OCS release potential within the basin.

Special contributions were made by Dr. Daniel W. Smith of Conestoga Rovers Consulting, Mr. Robert Bailey of Bailey Associates, and Mr. Larry LaFleur of the National Council of the Paper Industry for Air and Stream Improvement. Their in-depth presentations have provided insights into OCS formation and release chemistry as well as the state of OCS concentration in the Great Lakes ecosystem.

Partial financial support for the production of this report was provided by grants from U.S. EPA and Environment Canada.

Requests for copies of this report, or questions, should be directed to Mr. George Kuper, President and CEO, Council of Great Lakes Industries, PO Box 134006, Ann Arbor, MI 48113-4006, (734) 663-1944, FAX (734) 663-2424, e-mail:ghk@cgli.org.

This report and additional information regarding industry efforts towards implementation of the Great Lakes Binational Toxics Strategy can be found on the CGLI Website at <http://www.cgli.org>.

**Octachlorostyrene
and
Suggested Industrial Sources**

***A report to the Great Lakes Binational Toxics Strategy
OCS Workgroup***

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Octachlorostyrene and Suggested Industrial Sources

A report to the Great Lakes Binational Toxics Strategy OCS Workgroup

Executive Summary

As part of the Great Lakes Binational Toxics Strategy (BNTS) Octachlorostyrene (OCS) Workgroup effort to evaluate sources of octachlorostyrene and meet Strategy challenge goals, the Council of Great Lakes Industries (CGLI) has committed to:

- coordinate an industry review of suggested industrial sources of OCS,
- determine if these sources do exist within the Great Lakes Basin,
- if so, determine their status, and
- seek reduction commitments for significant sources.

This report provides a status report on the work begun to evaluate suggested sources.

The Study Approach

The approach to the OCS source review work was to:

- study information regarding suggested industrial sources and the basis for selecting them,
- review this information with knowledgeable persons within each sector, and
- provide perspective and reality check for the significance of potential sector releases through examination of OCS environmental concentration trend data.

The Findings

This work has produced the following findings.

- In many industry sectors, pollution prevention measures have eliminated or significantly reduced OCS releases.
- In other sectors, Great Lakes Basin located processes which had previously released OCS have been shut down.
- In a few sectors, continuing OCS releases, if they actually occur at all, are at very low, often not detectable, levels.
- The examination of OCS environmental trend data shows that concentrations are decreasing rapidly. They are at or approaching detection limits in most media. If remaining OCS sources were significant, it would be expected that environmental concentration trends would be reaching a plateau, or in the worst case scenario, increasing.

The Conclusions

Based on the sector by sector analysis results and environmental trend data described in this report it is concluded that, for the sectors for which we have data, contemporary industrial sources of OCS in the Great Lakes ecosystem have been virtually eliminated¹.

This status has been achieved through exercise of pollution prevention and pollution control measures.

The CGLI OCS Inventory Matrix

CGLI's initial efforts to collect source information were based on the Battelle Memorial Institute prepared Draft Action Plan for OCS (January 1998). To provide a guide for a source information gathering effort, a spreadsheet or Work Sheet matrix was constructed by CGLI and presented to the OCS Workgroup. Following publication of the second Battelle OCS report (November 5, 1998), it was revised to include some of the additional source information presented in that report. As is evident upon examination of the revised OCS Work Sheet, substantial information was required from many industrial sectors. The status of this effort is discussed in this report, sector by sector.

The OCS Suggested Source Decision Tree

Upon examination of the expanded suggested source picture presented by the second Battelle report, CGLI determined that a decision process would be needed to determine how to proceed with the pursuit of release reductions which will lead to attainment of the BNTS OCS challenge goals. This conclusion led to the recognition that if the technology was not in use within the industry or the Great Lakes Basin, no further information pursuit was necessary. Extending the logic through a stepwise thought process led to the decision tree which is explained and used in this report.

Canadian Inventory Efforts

The Ontario Section of Environment Canada has undertaken an effort to construct an OCS inventory for the Province. Like the second Battelle report it makes use of HCB/OCS ratios to calculate OCS releases. This approach is problematic, as is discussed within this report. However, unlike the Battelle report, the Ontario inventory project has made use of a decision tree-like process and relied on the existence of specific industrial processes within the Province as the key to whether or not OCS releases from that sector occur. Consequently, the February 17, 1999 draft inventory report concludes that "[s]everal suspected sources of OCS have been

¹ The primary focus of this study has been the Great Lakes Basin. However, also included in this report is information pertaining to the likelihood of OCS releases at St. Lawrence River watershed based (Quebec) magnesium production and copper recycling (electronic equipment) facilities. Emissions potential at both was found to be unexpected or small.

eliminated...” In addition, the report corrects reports that OCS may have been released from sectors such as the pulp and paper industry and rubber tire manufacturing.

Industry Sectors Contacted

Based on the sectors listed on the CGLI OCS Inventory matrix, contacts were identified and initiated. Information received ranges from OCS specific details to acknowledgment of receipt of information provided by CGLI and a commitment to follow-up and provide a response. The sector by sector review information presented in the report is summarized below.

Chlor-alkali Production:

The suggested source of OCS release from Chlor-alkali production is graphitic electrode process use. The Chlorine Institute is unaware of any U.S. chlor-alkali facilities that still use graphite anodes. The process is, likewise, no longer in use in Ontario.

Magnesium Production:

Magnesium industry personnel contacted by CGLI, in both the U.S. and Canada, have confirmed that graphitic magnesium production processes are used in a plant in Becancœur, Quebec. A new plant, which will also use an electrolytic process, is under construction in Asbestos, Quebec. It will employ pollution control equipment which will limit potential releases of OCS to the environment to very low levels.

PVC Incineration:

The assertion in the Battelle report that incineration of PVC materials represents a source of OCS is based on laboratory experiments which were designed to demonstrate that OCS could be formed. The report does not take into account the fact that incinerators are operated using combustion controls which avoid conditions favoring formation of dioxins and related compounds. The draft Canadian inventory report relates that OCS concentrations at the one municipal incinerator tested were not detected.

Metal Degreasing:

Chlorinated solvents have, for many years, been used to remove oils, greases, and other contaminants from metal parts. The draft Battelle report offers no data to support the contention that this process is a source of OCS, instead the report relies on the tenuous comparison to the aluminum degassing process. Most degreasing processes do not provide sufficient energy to facilitate the series of reactions necessary to produce OCS and are therefore inappropriately implicated. The report also fails to consider the fact that chlorinated solvent waste generated in the boiling sump of a vapor degreaser is subject to strict storage, handling, and disposal requirements under the U.S. hazardous waste regulations and therefore not released into the ecosystem.

Auto Fuel Combustion:

The Canadian Petroleum Products Institute has conducted a study which concluded that OCS is not present in tailpipe emissions or petroleum fuels.

Aluminum Production (Pri./Sec.):

Representatives of the aluminum industry report that hexachloroethane (HCE), alleged to produce OCS as a by-product, is no longer used in most primary aluminum degassing operations. No smelters in the Great Lakes Basin use HCE. Chlorine is used instead. The industry knows of no association between the use of this process and the production of OCS. No electrolytic processes are in use in the U.S.

PVC Coated Wire Recycling:

Vinyl Institute personnel have confirmed that open burning of wire for copper recovery is no longer an industry practice. As mentioned in the Battelle report, insulation is mechanically removed from scrap wire before recycling. Testing at a Quebec facility recycling electronic scrap found no significant releases of dioxin or styrene.

PVC Polymerization/Production:

The Vinyl Institute (VI) has no data showing that OCS is formed during the polymerization of vinyl chloride monomer (VCM). Although the report is not clear in this regard, it appears that EPA's speculation that PVC production is a source of OCS stems from an assumption that OCS is formed when polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F, or "dioxin") are formed, and that dioxin is formed during the polymerization of vinyl chloride. The VI does not believe that dioxin is formed during the polymerization process, and this conclusion is supported by the findings in the Vinyl Institute Dioxin Characterization Program Phase I Report (August 1998), which was previously submitted to EPA.

Pesticide Manufacture:

The practice of assuming a relationship between HCB presence and OCS presence in the pesticide manufacturing sector (or any other for that matter) should only be done when enough information is available to correctly determine the ratio on a case-by-case basis. Conditions which may produce HCB may or may not also produce OCS, or do so at differing ratios. In addition, it is inappropriate to base conclusions on HCB releases from pesticide manufacture or use on the basis of regulatory limits. Actual product HCB concentrations are significantly lower than maximum content limits set by registration authorities.

Pentachlorophenol Production/Wood Preservation:

The Pentachlorophenol Task Force, an industry group which provides data needed for continued registration of "penta" in the U.S., Canada and elsewhere, has no information confirming the

presence of OCS in “penta,” as is suggested in the Battelle OCS report.

Pulp and Paper Making/Chlorine Bleaching:

Pulp and paper mills are not thought to produce OCS or HCB. Details are provided by the industry. They conclude that pulp and paper making processes “have never favored formation of highly chlorinated substances.” OCS and HCB are, of course, very highly chlorinated materials. Conditions do not favor their formation in pulp mills. The draft Canadian inventory report confirms that OCS production which may have been associated with graphitic electrode based chlor-alkali production facilities is not now occurring. The process is no longer used in Ontario. The one on-site chlor-alkali facility operating at a Great Lakes Basin U.S. pulp and paper mill makes use of the diaphragm cell process and does not use graphite anodes.

Chlorinated Solvent Production:

Chlorinated solvent production does appear to have been a source of OCS contamination in the past. The draft Battelle report does not attempt, however, to evaluate changes in the manufacturing process over the last 10 to 15 years. As a result, the report bases its conclusions about potential releases from solvent manufacture on practices that are no longer applicable. Today, waste products from solvent production are either reused in other processes, incinerated, or placed in secure landfills, keeping them out of the ecosystem. Additionally, many of the facilities and processes from which the older OCS release data is cited have been shut down.

Coke Production:

Test results from Stelco Inc.’s Lake Erie Steel Company failed to detect OCS in coke oven emissions. Environment Canada has determined that the iron and steel sector is not a source of OCS and that an error had occurred in 1990 reporting activities which had suggested otherwise.

Tire Manufacturing:

Industry contacts explain that the assertion that tire tread compounds contain HCB (from which OCS suggested releases were calculated) comes from an April 98 report by U.S. EPA. It is based on analysis of tire tread compound which the industry has since found to have been reported in error. Additionally, EPA has historically reported the presence of chlorine in natural rubber. The industry has found no evidence that rubber contains chlorine.

Other Sectors:

CGLI is currently seeking information regarding these sectors:

- ***Chlorinated Solvent Incineration***
- ***PCB Incineration - Waste Oil Burning***
- ***Rare Metals Production***

The Status and Trends of OCS in the Environment

A review of OCS levels in the environment has been made to determine the significance of potential or suggested OCS sources which may remain in the Great Lakes Basin. The following questions were posed, data was studied, and conclusions reached:

- What are current concentrations of OCS in Great Lakes media?

Answer: Current levels of OCS in most media are now at the limit of detection or rapidly approaching this limit at most sites in the Great Lakes.

- How have concentrations changed over time?

Answer: Levels of OCS are decreasing significantly and, compared to other organochlorines, relatively rapidly, e.g., 8% to 30% per year.

- How do concentrations vary from place to place?

Answer: Gull egg data suggest that OCS burdens in Lake Huron, Lake Erie, and Lake Ontario are higher than in Lakes Superior and Michigan, although there is substantial intra-lake variability between colonies from Lakes Erie and Huron. Elevated concentrations appear to be related to historical sources.

- What can be deduced concerning current sources and future trends?

Answer: From atmospheric data, it appears that long range transport may be a vehicle for deposition of OCS in the Great Lakes ecosystem. However, based on the environmental trend data presented, this source is probably not significant.

Additional data are presented to substantiate the hypotheses that current concentrations of OCS are primarily based on internal loading from sediment inventories, based on previous loading. Sediment inventories are exhaustible and inexorably declining. Current external loading of OCS from sources within or outside of the Great Lakes basin are insignificant.

A Critical Review of the Second Battelle Report

OCS Formation Considerations:

The National Council of the Paper Industry for Air and Stream Improvement has studied the mechanics of chlorinated phenolic compounds extensively. Their review of the draft Battelle report has concluded that from a mechanistic and scientific process standpoint, the document is seriously flawed. A detailed analysis is provided.

Additional analyses have been conducted by Dr. Daniel W. Smith of Conestoga Rovers Consulting, and Mr. Robert Bailey on behalf of the Chlorine Chemistry Council. They have concluded that the primary Battelle approach was to summarize what information they found on occurrence of OCS in the environment and potential sources. However, there was no segregation of the data by time so that the conclusions are based in large part on older information, reflecting technology and practices from the 1970s and earlier. Data from one and two decades ago are presented as if these data reflected current levels and current sources. In depth trends analyses presented in the discussion which follows demonstrate that OCS concentrations are falling, at a half-life rate of between 3 to 7 years. In addition, surrogates were incorrectly used to estimate OCS emissions and concentrations in the environment. The draft conclusion that OCS may be

currently emitted in significant quantity in the Great Lakes region is not supported by either the current analyses for OCS in the environment or correctly calculated emission estimates based on surrogates.

Octachlorostyrene and Suggested Industrial Sources

A report to the Great Lakes Binational Toxics Strategy OCS Workgroup

Introduction

As part of the Great Lakes Binational Toxics Strategy (BNTS) Octachlorostyrene (OCS) Workgroup effort to evaluate sources of octachlorostyrene and meet Strategy challenge goals, The Council of Great Lakes Industries (CGLI) has committed to:

- coordinate an industry review of suggested industrial sources of OCS,
- determine if these sources do exist within the Great Lakes Basin,
- if so, determine their status, and
- seek reduction commitments for significant sources.

This report provides a status report on the work begun to evaluate suggested sources.

The starting point for this work was the January 1998 Draft Action Plan for Octachlorostyrene prepared for the workgroup, at the request of U.S. EPA Region 5 personnel, by Battelle Memorial Institute. Sources suggested in the Draft Action Plan were categorized and logged into a spreadsheet matrix to serve as a road map for tracking down information regarding industry sectors, processes, and individual companies to determine release status.

To determine the basis for the listing of Action Plan suggested sources, literature references used to support the January 1998 paper were requested from Battelle. Copies of the papers were obtained and reviewed¹.

Just prior to the November 16, 1998 Chicago Binational Toxics Strategy Stakeholders meeting, a second Battelle report was released by U.S. EPA Region 5. It included a new, much expanded, list of literature references and suggested additional industrial sources². It made use of an

1 Of the 18 original references, half of them did not pertain to OCS production or release. It is unclear why these references were chosen. They do not appear to be relevant. Of those references which do pertain to OCS, three draw conclusions regarding releases by extrapolating backwards from sediment data, two report results from laboratory combustion studies deliberately designed to produce chlorinated off-gases, two of these report the identification of compounds emitted tentatively as OCS, and one demonstrated OCS release potential from aluminum processing through laboratory experiments. Only one paper actually reports a documented OCS release. In that case, a landfill leachate test proved positive for OCS while a concurrent effluent sample did not.

2 The second Battelle report includes a list of 107 references which are said to pertain to the release and/or environmental fate of OCS. Of the 107, nine are those which were included in the original list of 18 and which do pertain to OCS. The 9 irrelevant references have been screened out. However, given the nature of the original references (the fact that only one actually documents a release), the new longer list must be examined carefully. Some or several may not substantiate actual OCS release activity. CGLI has requested assistance from Region 5 and Battelle personnel in locating copies of the references.

assumed relationship between hexachlorobenzene (HCB) and OCS releases. If HCB releases had been detected from given sources, OCS was assumed to have also been released. Attempts were made to quantify OCS releases on the basis of sediment calculated release factors.

This report provides a status report on the work begun to evaluate suggested sources from the first OCS report, the Draft Action Plan. The source list has been updated somewhat on the basis of clarifying information contained in the second Battelle report. However, the additional sources, especially those which appear to be theoretically based and depend on HCB or other chlorinated compound associations have not, at this time, all been added to the CGLI OCS source matrix.

In addition to the original Battelle Draft Action Plan, Environment Canada has produced an OCS inventory as part of their reporting activities supporting the Canada-Ontario Agreement (COA). This report also addresses sources listed in the COA report.

The CGLI OCS Inventory Matrix

To serve as a guide for identification of source information gathering, a spreadsheet or matrix was initially constructed by CGLI and presented to the OCS Workgroup. It listed the suggested sources as described in the Draft Action Plan. Contact points were established for each of the suggested sources and provided opportunities to record reference data, release information, and reduction commitments. Upon review of the second Battelle OCS report, CGLI revised the matrix. The suggested source categories were sectorized and specific sector processes upon which OCS releases had been based or suggested were included. This refinement was made to expedite industry contact and information gathering. The revised source matrix appears in Appendix I.

The revised matrix utilizes the decision tree information gathering and source management concept. This approach, described below, will simplify the assessment of the suggested sources and focus efforts and attention on those which are significant from the standpoint of meeting the BNTS OCS challenges. Decision information for sectors for which data has been collected has been included in the Appendix II presentation.

As is evident upon examination of the revised OCS Work Sheet, substantial information must still be obtained from many industrial sectors. This data collection effort is, and has been, underway for some time. The status of this work is discussed, sector by sector, below.

The OCS Suggested Source Decision Tree

Upon examination of the expanded suggested source picture presented by the second Battelle report, CGLI determined that a decision process would be needed to determine how to proceed with the pursuit of release reductions which will lead to attainment of the BNTS OCS challenge goals.

The decision tree approach derived is shown in Appendix II. The basis for this approach came from the fact that both of the Battelle reports are based on very old reference information. Papers and assessments of industrial process dating to the 1980's are used to draw conclusions regarding documented OCS releases or theoretical OCS production. Industry has been in the process of phasing out older technologies. Therefore, it was determined that a logical first step is to determine if a technology which has been linked with OCS production is still in use. This conclusion led to the recognition that, if the technology was no longer in use within the industry, no further information pursuit was necessary. Likewise, if the technology is in use but not in the Great Lakes Basin, further pursuit may not be necessary. Extending the logic through a stepwise thought process led to the decision tree.

Canadian Inventory Efforts

The Ontario Section of Environment Canada has undertaken an effort to construct an OCS inventory for the Province. Like the second Battelle report it makes use of HCB/OCS ratios to calculate OCS releases. This approach is problematic, as is discussed within this report. However, unlike the Battelle report, the Ontario inventory project has made use of a decision tree-like process and relied on the existence of use of specific industrial processes as the key to whether or not OCS releases from that sector occur. Consequently, the February 17, 1999 draft inventory report concludes that “[s]everal suspected sources of OCS have been eliminated, including the production of chlorine, chlorinated solvents, vinyl chloride/ethylene dichloride/PVC, pentachlorophenol, and pesticides. These were eliminated largely because such operations are not conducted in Ontario.”

In addition, the report corrects reports that OCS may have been released from sectors such as the pulp and paper industry and rubber tire manufacturing. While much more extensive review of this new draft report is needed, especially relative to the use of surrogate ratios for release quantity estimates, the approach of concluding that Basin “sources” do not exist when the technology is not practiced within a sector or the Basin is the correct one. Also, these inventory reviews should “correct the record” when evidence is available showing that “sources” have been named in error.

Industry Sectors Contacted

Based on the sectors listed on the CGLI OCS Inventory matrix, industry contacts were identified and initiated. A listing of the sectors contacted appears in Table 1. The table indicates sectors targeted for contact in both Canada and the U.S. It also indicates which contacts have resulted in responses. In some cases, the responses are preliminary and follow-up information will be forthcoming. In only a few cases, the correct point of contact has not yet been established. We are continuing to pursue these contacts and report on them when the needed information has been collected.

Table 1

**Industry Sectors Contacted
Regarding OCS
Release Information**

Sector	Canada	U.S.	Response Received	
			Canada	U.S.
Chlor-alkali Production	X	X	X	X
Magnesium Production	X	X	X	X
Vinyl Production	X	X		X
Oil Recycling	X	X		
Auto Fuel Production	X	X	X	
Auto Fuel Use	X	X	X	
Chlorinated Solvent Production	X	X	X	X
Aluminum Production (Pri/Sec)	X	X	X	X
Pesticides Manufacture	X	X	X	X
Pesticides Use	X	X	X	X
Wood Preservation		X		X
Pulp and Paper Manufacture	X	X	X	X
Coke Production	X	X	X	X
Waste Disposal - Incineration	X	X		
Cement Kiln Recycling	X	X		
Tire manufacturing	X	X		X

Sector Responses

As mentioned above, most sector contacts have provided responses. As noted in Table 1 and at the end of this section, a few sectors have not yet reported back to CGLI. These responses will be forwarded to the Workgroup when received.

One common response has been that OCS releases have not been previously associated with the suggested industry sectors or processes, and little or no data is available. In addition, MACT regulations are currently under development for VOCs as a class, but not for individual compounds. MACT standard development data is commonly collected for aggregated VOC compounds, not specific compounds such as OCS. Sector contacts are researching databases and emissions reports for additional information.

A sector-by-sector summary of the information obtained so far is provided in the paragraphs which follow.

1 Chlor-alkali Production:

The suggested source of OCS releases from Chlor-alkali production is graphitic electrode process use. The Chlorine Institute is unaware of any U.S. chlor-alkali facilities that still use graphite anodes. The Institute relates that the use of these anodes was common prior to the advent of metal anodes. Contacts with individual producers confirm that these conversions have been made. In fact, many were done during the late 1960's. By the late 1980's all conversions are believed to have been accomplished. One incentive for completing the conversions was a significant cost savings over the older graphite electrode process. The process is, likewise, no longer in use in Ontario. Using the decision tree concept. It is not necessary to pursue OCS releases from graphitic electrode chlor-alkali production facilities any further since the technology is not in use.

"Questions" regarding carbon containing membrane cell chlor-alkali production processes, raised in the second Battelle OCS report are of the "theoretical" nature. There are substantial differences between the electro-chemistry of a diaphragm cell utilizing graphite anodes vs. the chemistry in the membrane cell process. Suggestions that OCS may be produced just because carbon may be present is a substantial stretch. There has been no confirmation that OCS is produced in these cells.

2 Magnesium Production:

Magnesium industry personnel contacted by CGLI have confirmed that no graphitic processes are currently used in the Great Lakes Basin. One such facility is located in Becancoeur, Quebec, in the St. Lawrence River watershed. Another is under construction in Asbestos Quebec.

An environmental assessment was conducted on the proposal to build the Asbestos plant. Chlorine will be evolved in the electrolysis stage where chlorinated hydrocarbons (CHCs) will also be generated. The gas will be used to regenerate hydrochloric acid which will collect most of the

CHCs. Air emissions of dioxins and furans from the facility are expected be 0.09 g/y TEQ. CHC levels in the leach residue will be controlled by carbon adsorption from the return acid. The residue will contain approximately 20 g/y TEQ at a concentration of 66 pg/g TEQ and will be stored in a secure impoundment. All pond water will be returned to the process which will have no liquid discharge to the environment. Carbon filter material will be sent to an off-site hazardous waste facility for disposal by incineration.

OCS is included in the environmental monitoring program for the facility. While there can be no assurance that there will be no OCS releases, it is anticipated that the CHC control measures will limit potential releases of OCS to the environment.

A Utah based producer is currently evaluating dioxin and/or HCB release potential from their graphitic operation. State of Utah environmental agency personnel are participating in the study. The generation or release of OCS has not been a concern at this facility and is not a part of this study.

3 PVC Incineration:

The assertion in the Battelle report that incineration of PVC materials represents a source of OCS is based on laboratory experiments which were designed to demonstrate that OCS could be formed. The report does not take into account the fact that incinerators are operated using combustion controls which avoid conditions favoring formation of dioxins and related compounds. The draft Canadian inventory report relates that OCS concentrations at the one municipal incinerator tested were not detected.

The Battelle report suggests that PVC products that are land-disposed rather than recycled or incinerated can be potential sources of OCS if accidental landfill fires occur. At the same time, the report indicates that all incineration processes involving chlorinated substances should be expected to form OCS. Studies on dioxin emission from commercial incineration systems indicate that the control of combustion conditions is the most effective way to minimize dioxin emissions.³

It is reasonable to conclude that this technology would also be effective in the mitigation of OCS emissions. Further, modern landfill management practices mitigate the potential for landfill fires.

4 Metal Degreasing:

The Halogenated Solvents Industry Alliance, Inc. has reviewed the portion of the Battelle report which suggests that OCS may be released by metal degreasing operations. Their response to this assertion is:

Chlorinated solvents have, for many years, been used to degrease oils, greases, and other contaminants from metal parts. In the typical process, the solvent is heated to its boiling point and the contaminants are flushed by the solvent vapors as they condense on the part

³ See, e.g., "The Relationship Between Chlorine in Waste Streams and Dioxin Emissions From Waste Combustor Stacks," H. Gregor Rigo, *et al.*, American Society of Mechanical Engineers (1995).

in the vapor zone. To ensure effective cleaning, contaminants are periodically removed from the boiling sump and disposed of as hazardous waste.

In its discussion of metals degreasing, the draft report suggests that:

As in aluminum degassing, the reaction of chlorinated solvents with carbon deposits on the metal at elevated temperatures *may* generate OCS as a byproduct in the contaminated solvent drained from the machine or in the organic impurities that accumulate in the sump.
(*emphasis added*)

The draft offers no data to support this contention, instead relying on the tenuous comparison to the aluminum degassing process. In the information provided for degassing, however, the draft notes that the production of OCS has been found to occur at 600°C. As indicated previously, the temperatures routinely encountered in the sump of a vapor degreasing are around the boiling point of the solvent (121°C or less). Clearly, the degreasing process does not provide sufficient energy to facilitate the series of reactions necessary to produce OCS. Even in a poorly maintained degreaser, where contaminated sludge has accumulated on the heating coils in the boiling sump and temperatures may rise above the boiling point, safety controls required on the equipment shut off the heat supply well below the temperatures encountered in aluminum degassing.

The report also fails to consider the fact that chlorinated solvent waste generated in the boiling sump of a vapor degreaser is subject to strict storage, handling, and disposal requirements under the nation's hazardous waste regulations. These wastes may not be discarded in a landfill and generally are destroyed in hazardous waste incinerators or cement kilns. To the extent that destruction of degreaser wastes may contribute to release of OCS, the report already addresses them in its consideration of incineration processes.

5 Auto Fuel Combustion:

The Canadian Petroleum Products Institute, through its National Toxic Substances Task Force (TSTF) carried out an extensive worldwide survey and assessment of "chemical emissions from vehicle tailpipes." This two phase study consisted of a detailed literature search of all known vehicle tailpipe emission databases. Phase 1 of the study was completed in 1997 with the report published in November 1997. Phase 2 is currently being completed. Octachlorostyrene was not detected in any of the studies, and the experts concluded that it would be very unlikely to find the substance in tailpipe emissions. Discussions with refinery experts also confirmed that the substance is unlikely to be found in petroleum products.

6 Aluminum Production (Pri./Sec.):

Representatives of the aluminum industry report that hexachloroethane (HCE) is no longer used in most primary aluminum degassing operations. Additionally, no smelters in the Great Lakes Basin use HCE. Chlorine is used instead. The industry knows of no association between the use

of this process and the production of OCS. However, as part of a MACT rule development study, the quantity of chlorine used for this purpose has been reduced to control chlorine, HCl, dioxin and furan releases from the process. If OCS were produced, these process changes would also result in lower releases of all volatile compounds, including any OCS which might be present. New MACT standards for these sources are expected to be finalized by U.S. EPA by December 31, 1999. A three year compliance period will be provided, assuring that the sought after reductions will have been made by year 2003. Many facilities control volatile emissions through use of lime injected baghouses. This equipment is expected to further reduce releases.

A separate primary MACT standard, which became final in 1997, addresses Particulate aromatic organic matter. A three year compliance period will produce PAOM reductions of at least 50%. The only Great Lakes Region facility, a State of New York plant, is "fast tracking" PAOM MACT reductions. All other facilities in the region use a "prebake" process which produces much lower PAOM emissions.

The secondary aluminum industry is also subject to new MACT standards. These standards require that old cans be delacquered before melting. In addition to the new standards, the industry has moved away from direct melting practices because of low recovery experience.

Any estimate of OCS releases from the aluminum sector must consider the impact these changes have had, and will have, on final quantities.

Finally, Aluminum Industry personnel have related that no electrolytic processes are in use in the U.S.

7 PVC Coated Wire Recycling:

Vinyl Institute personnel have confirmed that open burning of wire for copper recovery is no longer an industry practice. As mentioned in the Battelle report, insulation is mechanically removed from scrap wire before recycling.

Investigations at a Quebec⁴ primary copper smelting facility which recycles electronic scrap was tested for dioxin, furan, and styrene emissions. At plastic feed rates four or five times normal production rates, dioxin/furan releases did not exceed 0.1 grams TEQ per year. Styrene was not detected in an acidic waste stream which would have concentrated the material at detection limits ranging from 0.01 to 6 ug/l.

This sector does not appear to produce significant quantities of OCS.

⁴ This facility located in Northwestern Quebec would be unlikely to influence environmental quality with the Great Lakes Region, but monitoring results may be of relevance in assessing potential releases from copper smelters.

8 PVC Polymerization/Production:

The Vinyl Institute (VI) has no data showing that OCS is formed during the polymerization of VCM⁵. Although the report is not clear in this regard, it appears that EPA's speculation that PVC production is a source of OCS stems from an assumption that OCS is formed when polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F, or "dioxin") are formed, and that dioxin is formed during the polymerization of vinyl chloride. The VI does not believe that dioxin is formed during the polymerization process, and this conclusion is supported by the findings in the Vinyl Institute Dioxin Characterization Program Phase I Report (August 1998), which was previously submitted to EPA.

The OCS Report states that the formation of OCS in the PVC polymerization process "is not certain". From a chemistry perspective, we have no reason to believe that any perchlorinated species are created in the vinyl chloride polymerization process. Thus, the report's conclusion should be revised to state that OCS is not predicted to be formed during the polymerization process.

9 Vinyl Manufacturing Process

Likewise, OCS formation would not likely occur in the ethylene dichloride EDC cracking process for the manufacturing of vinyl chloride monomer (VCM). If OCS is formed as a minor, inadvertent, byproduct in the VCM process, its formation would likely occur further downstream. As acknowledged in the report, OCS is not deliberately manufactured, and the vinyl industry does not use OCS in any form. Further, based on knowledge and experience, any OCS that is unintentionally manufactured would be captured in the EDC or VCM purification process and/or emission control devices, which are strictly regulated under the Clean Air Act (CAA), Clean Water Act (CWA), and the Resource Conservation and Recovery Act (RCRA) to control emissions of hazardous air pollutants and other substances. As the OCS Report itself notes that "[t]here are no emissions released directly to the atmosphere [from EDC and VCM production facilities], as regulations require emission sources to be enclosed and all emissions to be collected." Report at 41 (emphasis added).

As the report notes, gaseous streams are treated by incineration and liquid streams and wastewater are stripped of trace organics. In this regard, it is also important to note that incineration at EDC/VCM facilities, as well as PVC production facilities, is highly regulated and subject to continuous emissions monitoring. The incinerator operating parameters at these facilities provide a high degree of assurance. Further, the trace organics stripped from wastewater are typically routed back into the production process or to a well-controlled incinerator.

Because the industry has little or no releases of OCS, the VI has not developed data on emissions of OCS from the vinyl manufacturing process. However, a worst case estimate can be

5 VI's members include: Borden Chemicals and Plastics Limited Partnership, CertainTeed Corporation, CONDEA-Vista Company, The Dow Chemical Company, Formosa Plastics U.S.A., The Geon Company, Georgia Gulf Corporation, Kaneka Delaware Corporation, Occidental Chemical Corporation, PPG Industries, Inc., Shintech, Inc., Union Carbide Chemicals and Plastics, and Westlake PVC Corporation.

constructed based on industry data and the OCS/dioxin ratio presented in the report. Please note that we have no basis to support the ratio factor of 653 for OCS to dioxin described in the report.⁶ Report at A-4. We use that figure here only to support the conclusion that the report should state that the vinyl industry is not a source of OCS.

If we assume that a relationship between the formation of dioxin and the formation of OCS in the EDC/VCM/PVC process exists, we can begin by basing an emissions estimate for OCS on dioxin emissions. In its August 1998, Dioxin Characterization Phase I Report, the vinyl industry indicated that the only potential release points of dioxin in the PVC manufacturing process were the incineration of the vinyl chloride recovery process vent, emissions from the polymer dryers, and wastewater. The recovery process vent is regulated under the CAAs National Emission Standards for Hazardous Air Pollutant Emissions (NESHAP) to comply with a 10 parts per million (ppm) VCM emission limit in the vent stream.⁷ For EDC/VCM production, dioxins were found in emissions from the process vent incinerators and wastewater, which are also regulated.

The report should note that the production of 12.5 billion pounds of PVC and 13.6 billion pounds of VCM from 25.5 billion pounds of EDC per year generates less than 31.3 grams on a Toxic Equivalent (TEQ) basis per year of dioxins to air and less than 0.22 grams TEQ/year of dioxins to water. As noted above, although we have no basis to support the ratio factor of 653 for OCS to dioxin that is described in the OCS Report, OCS emissions based on the suggested ratio of OCS concentrations to dioxin emissions can be estimated. Applying the ratio factor, total U.S. EDC/VCM/PVC production would emit less than 20.4 kilograms per year (kg/y) of OCS to the air and less than 0.143 kg/y of OCS to water. In addition, these would be *total* national release numbers and would not reflect actual releases or deposition in the Great Lakes basin. The VI study found that over 98 percent of estimated dioxin releases originated from facilities that manufacture EDC/VCM or EDC/VCM/PVC, which, as noted above, are not located in the Great Lakes region. In sum, given EPA's estimate of 4,157 pounds (1,890 kg) per year emissions of OCS, the calculated worst case for the EDC/VCM/PVC industry contribution is so small as to be inconsequential.

Finally, members of VI are responsible for the majority of the domestic production volume of EDC, VCM, and PVC. However, the vinyl industry has a limited presence in the Great Lakes Basin. All production of EDC and VCM in the U.S. occurs in Kentucky, Louisiana, and Texas. EPA itself acknowledges that there are no EDC/VCM production facilities in the Great Lakes Basin. Report at 53. In addition, more than 90 percent of U.S. PVC production occurs outside of the Great Lakes states. Indeed, the report only identifies a single location for PVC polymerization in the Great Lakes Basin. (Report at 54) **This facility has been closed.** EPA is also considering the potential for atmospheric deposition to be a source of OCS contamination in the Great Lakes Basin. However, EDC, VCM, and PVC production facilities are geographically located such that atmospheric deposition in the Great Lakes is so unlikely that it is reasonable to

⁶ The lack of an asserted correlation between a specific dioxin/furan congener and OCS adds further uncertainty to the OCS/dioxin ratio. This is particularly important since the small amounts of dioxin and furans produced in the EDC/VCM manufacturing process predominantly are the more highly chlorinated, less toxic species, such as octachlorodibenzo-p-dioxin.

⁷ 40 C.F.R. Sec. 61.60 *et. seq.*

conclude that the industry is not a source of OCS in the Great Lakes region. This conclusion is supported by the history of OCS contamination in Lake Ontario sediments and in Lake Ontario trout. The report reflects decreasing OCS levels, approaching the near-zero level between 1921 and 1981. Report at 20. Similarly, concentrations of OCS in trout declined from 263 nanograms per gram in 1977 to 31.3 ng/g in 1993. During these periods of declining OCS releases to the environment, U.S. production of EDC, VCM, and PVC increased substantially to more than 25, 13, and 12 billion pounds a year, respectively. If the EDC/VCM/PVC industry was a source of OCS in the Great Lakes Basin, this would have been reflected in actual monitoring data.

10 Pesticide Manufacture:

The practice of assuming a relationship between HCB presence and OCS presence in the pesticide manufacturing sector (or any other for that matter) should only be done when enough information is available to correctly determine the ratio on a case-by-case basis if such a ratio exists, and if so, what it might be. Conditions which may produce HCB may or may not also produce OCS, or do so at differing ratios. (For details see Critical Review of Battelle Report presentation provided below.) However, since OCS data are not available, the following surrogate information is presented.

HCB can be produced as a trace byproduct in many reactions where chlorine and carbon are present. Thus, it has been produced as a waste product from the production of many chlorinated chemicals. In the USA and Canada, this waste is either incinerated or placed in secure underground facilities. None of the facilities listed in the US Toxics Release Inventory which release HCB are located in the Great Lakes region.

HCB has been present as a microcontaminant in some chlorinated pesticides. Manufacturers have made process and raw material changes which have dramatically reduced or eliminated HCB concentrations. EPA regulates the maximum concentration of HCB possibly present in the pesticides as shown in Table 2. Current manufacturing methods produce materials with average HCB concentrations well under those listed in Table 2.

For example, atrazine producers confirm that HCB levels in their product are nearly always not detectable. One producer explains that “the average HCB level for a typical production campaign is < 1 ppm.” “[T]he maximum hexachlorobenzene content found in atrazine technical was 9.7 ppm....” Therefore it would be wrong to assume that chlorinated contaminants are present in pesticides at their respective regulatory levels. This information, the fact that pesticides are not applied as “neat” material straight from the drum, in consideration of the declining application rates now used for pesticide products, all lead to the conclusion that contaminant levels resulting from pesticide production or use are not significant.

Table 2.
Regulatory Levels for HCB as a Contaminant in Pesticides

Product	Maximum HCB concentration
Dimethyltetrachloro-terephthalate	1000 ppm
Atrazine	40 ppm
Simazine	40 ppm
Picloram	50 ppm
Pentachloronitrobenzene	500 ppm
Chlorothalonil	40 ppm
Lindane	100 ppm

11 Pentachlorophenol Production/Wood Preservation:

The Pentachlorophenol Task Force (PTF), an industry group which provides data needed for continued registration of “penta” in the U.S., Canada and elsewhere, has no information confirming the presence of OCS in penta, as is suggested in the Battelle OCS report. Comprised of the two U.S. registrants of penta, Vulcan Chemicals and KMG-Benuth Inc., the PTF is committed to ensuring that regulatory decisions regarding penta are based on sound science and reflect current, up-to-date-data.

Page 50 of the draft Battelle report states that the production of penta is suspected of forming OCS as a byproduct in trace amounts. A citation to Kirk-Othmer 1996 is given in support of that statement. The authors of the Battelle report attempt to draw a parallel between PCDD/PCDF formation during penta manufacture and OCS formation. Indeed, Table 4 in the draft report goes so far as to suggest that the amount of penta used annually to treat utility poles may contain up to 16,325,000grams of OCS. Based on roughly the 17 million pounds of penta being produced annually by PTF member companies, the figure in the Table would translate to an OCS content in penta of approximately 0.4 percent.

As indicated above, PTF members have no information confirming the presence of OCS in penta, as suggested in the second draft Battelle report. Nonetheless, we fail to see the scientific rationale for drawing a connection between the formation of trace quantities of certain higher chlorinated PCDDs/PCDFs during penta manufacture with any possible OCS formation. PTF members have examined the Kirk-Othmer reference and fail to see how it supports the contention of the report. Moreover, the suggestion that penta contains up to 0.4 percent OCS is plainly wrong. PTF member Vulcan has analyzed its penta for the presence of any contaminants at levels above 0.1 percent and OCS has not been identified.

12 Pulp and Paper Making/Chlorine Bleaching:

CGLI has contacted representatives of the pulp and paper industry regarding the suggested release of OCS [and Hexachlorobenzene (HCB)] from pulp and paper making processes. OCS

and HCB have **not** been detected in mill wastestreams. In addition, there is no evidence to support the contention that mills release OCS or HCB.

Details are provided in a February 1992 report prepared by the Water Resources Branch of the Ontario Ministry of the Environment⁸ and in the discussion which follows in the section of this report entitled “Critical Review of the Battelle Report.”

The OME letter explains that the only indication of OCS or HCB release was contained in a single report from the Ontario Ministry of Energy and Environment, which reported MISA monitoring data. Upon investigation, NCASI learned that “the preliminary data upon which the estimates are based were rejected from the MISA database after QA/QC review found sufficient irregularity in them to make it very doubtful that the mills were actually emitting the compounds.”

In addition, NCASI consulted with pulp and paper chemistry specialist Dr. Douglas Reeve of the University of Toronto. Dr. Reeve examined the chemical reactants and conditions necessary to produce OCS and HCB and compared them with pulp and paper making process conditions. He concluded that pulp and paper making processes “have never favored formation of highly chlorinated substances. The use of high or complete substitution of elemental chlorine with chlorine dioxide reduces the tendency even further.” OCS and HCB are, of course, very highly chlorinated materials. All U.S. mills will soon be converted to complete chlorine dioxide substitution in compliance with EPA’s new CLUSTER rule for this sector. This process is also commonly used at Canadian mills. Conditions have not favored the formation OCS and HCB in pulp mills. The recent and continuing conversion to the complete substitution process moves process conditions even further away from the likelihood that these compounds would be formed.

PCDD/F releases in pulp mill discharges have been an issue in the past. Mr. Larry LaFleur, a National Council of the Paper Industry Air and Stream Improvement (NCASI) Fellow, has reviewed the mechanisms necessary for OCS formation in the “Critical Review of the Battelle Report” section of this report. His review of the chemistry involved in bleaching processes, the mechanisms necessary for OCS formation, and extensive EPA sampling and monitoring efforts in a variety of bleaching processes where evidence of occurrence of potential OCS mechanisms would have been evident, have shown that there is “no justification for extrapolating from the historical presence of PCDD/F in pulp bleaching to the potential for this process to produce OCS⁹.”

13 Chlorinated Solvent Production:

The Halogenated Solvent Industry Alliance (HSIA) reports that:

Chlorinated solvents production does appear to have been a source of OCS contamination in the past. The available data cited in the draft report indicate that OCS can be produced

⁸ Report on the Analysis of the Quality Assurance and Quality Control Data for the MISA Pulp and Paper Sector, Water Resources Branch, Ontario Ministry of the Environment, February 1992, PIBS 1846, Log 91-2310-038.

⁹ See the discussion starting on page 37 of this report.

during the manufacture of chlorinated solvents and that OCS has been detected in the effluent from solvent manufacturing operations in studies conducted in the 1980s or earlier. The draft report does not attempt, however, to evaluate changes in the manufacturing process over the last 10 to 15 years. As a result, the report bases its conclusions about potential releases from solvents manufacture on practices that are no longer applicable. Today, waste products from solvent production are either reused in other processes, incinerated, or placed in secure landfills. According to information provided by EPA's Office of Pollution Prevention and Toxic Substances, moreover, OCS is largely dependent on the process used to produce the solvent.

Rather than use current data on OCS in solvent production effluent or, even, data that were collected in the 1970s or 1980s, the draft report bases its estimate for OCS on estimates of HCB releases from solvent production. This approach is significantly flawed for two reasons. The draft report provides no rationale to support its assumption that the ratio of OCS to HCB in releases of solvent production will be the same as the ratio found in sediment. The April 1998 estimates for HCB releases used in the draft, moreover, are greatly exaggerated.

Appendix A of the draft report provides a table of OCS/HCB ratios found in sediments that have been reported in the literature. A review of this table suggests that the ratio varies considerably, even among samples taken in the same area at the same time. It is reasonable to suspect, based on the information, that there may be processes that differentially alter the concentration of one pollutant relative to the other. Pereira et al (1988), in fact, suggest a "salting-out" effect in the Bayou d'Inde area to explain differences in levels found in sediments and water. Despite the variation in the reported ratios, the draft report offers no rationale for using the ratio found in sediment or for selecting the average of all of the reported ratio information.

Although HSIA does not necessarily disagree with the use of an OCS/HCB ratio for estimating potential releases, we believe that the ratio should be based on actual measurements from waste streams. HSIA notes that pollutant information is available from samples of waste streams from production facilities in Ontario and Louisiana.

Use of the OCS/HCB ratio also depends, of course, on the accuracy of the estimate for HCB. HSIA has submitted comments to EPA's Air Office concerning the flaws in the April 1998 inventory for HCB, the source used by the draft report. To summarize our comments, EPA's inventory analysis uses Toxic Release Inventory (TRI) reporting data from a small number of facilities and extrapolates these data to all U.S. facilities based on production capacity rather than actual production.

HSIA believes that TRI data overestimate actual emissions because they are based on theoretical (worst-case) calculations, rather than actual measurements. In reviewing the TRI data for 1996, however, we find a total of 451 pounds of HCB reportedly released to the environment (250 pounds to water, 201 pounds to air) from manufacturers of chlorinated solvents. We suggest that this is a more accurate estimate to use as a basis for

estimating OCS releases than the figure reported in EPA's April 1998 inventory.

Based on the above discussion the estimated OCS release rate reported by the Battelle report is at least 2000 times too high. The actual release rate, especially that to the Great Lakes Basin, is not thought to be significant.

14 Coke Production:

Test results from Stelco Inc.'s Lake Erie Steel Company failed to detect OCS in coke oven emissions. Environment Canada has determined that the iron and steel sector is not a source of OCS. An error that occurred in 1990 reporting activities suggested otherwise.

The "no source" conclusion is based on the fact that the Ontario government tested integrated steel plant effluents in 1989 and 1990 for various pollutants including OCS as part of its Municipal/Industrial Strategy for Abatement (MISA). OCS was not detected at any facility including Stelco Inc.'s Lake Erie Steel Company, which produces over 600,000 tons of coke annually. The effluent tested measured less than 0.0026 ug/l OCS (i.e. below detection limit). The RMDL was 0.010 ug/l.

15 Waste sites:

The second Battelle report discusses potential OCS releases from closed or active landfills. EPA's Vicki Thomas has said that these area sources would be dealt with as other aspects of the Binational Toxics Strategy. This direction and the fact that these potential sources are part of ongoing RCRA regulation and remediation programs precludes the consideration of confirmed, unconfirmed, or suspected OCS releases from waste sites as an industry source. This sector discussion should be removed from the Battelle report.

16 Tire Manufacturing:

OCS release from the tire manufacturing sector is suggested by the Battelle report based on reports that natural rubber contains HCB. Industry contacts explain that this assertion comes from an April '98 report from EPA, based on analysis of tire tread compound which industry has determined to have been in error. In addition to spurious results relating to HCB, the presence of carbon disulfide and toluene were also reported to EPA. These, too, have not been found in industry follow-up tests. The quantity of HCB reported to EPA was small, leading to the proposal of an AP-42 emission factor of 9.29×10^{-9} . Because the factor is so small, industry has not vigorously attempted to correct this error. However, if this insignificant quantity is to be pursued in light of BNTS challenge goals, the record must be corrected. Additionally, EPA has historically reported the presence of chlorine in natural rubber. This may lead to speculation regarding a potential for the formation of chlorinated compounds in rubber products. The industry has found no evidence that natural rubber contains chlorine. Contacts report that there is no data which directly links rubber products, or raw materials, to OCS.

Other Sources:

CGLI continues to seek information regarding suggested OCS releases in the following sectors.

- **Chlorinated Solvent Incineration**
- **PCB Incineration - Waste Oil Burning**
- **Rare Metals Production**

Information received from these contacts will be relayed to Environment Canada and U.S. EPA at a later date.

The Status and Trends of OCS in the Environment

17

To confirm the lack of significance of the potential or suggested OCS sources which may remain in the Great Lakes Basin, a review of the status of OCS levels in the environment has been made by Dr. Daniel W. Smith of Conestoga Rovers Consulting. The following analyses reviews his findings regarding the current status and spatial and temporal trends of octachlorostyrene (OCS) in Great Lakes media. These questions were addressed:

- What are current concentrations of OCS in Great Lakes media?
- How have concentrations changed over time?
- How do concentrations vary from place to place?
- What can be deduced concerning current sources and future trends?

Methods: Data on OCS concentrations in Great Lakes media were collected from available sources. Emphasis was placed on analyses of data sets that were extensive and relatively consistent in terms of methods of collection and chemical analyses. While some of the data have been published, most recent data were sought and obtained from various agencies. The Canadian Wildlife Services (CWS) supplied more recent data from that agencies long range monitoring of colonial bird eggs. The Ontario MOE supplied recent data on OCS concentrations spottail shiners from the Niagara River. Unpublished data from MOE's monitoring of water and suspended solids in the St. Clair and Niagara Rivers were obtained from MOE. The USEPA supplied unpublished data on OCS concentrations in Lake Ontario, collected by the EPA.

Temporal trends were analyzed based on the model of first order decline

$$C_t = C_0 * \exp^{(rt)}$$

Where C_t is the concentration at time t , C_0 is the concentration time 0 or the start, and r is the first-order rate constant. First-order decline assumes that proportional rates of decline are constant over time, that is

$$\frac{dC}{C dt} = \text{constant}$$

First order decline is the most appropriate model for decline of persistent chemicals in the environment because the fate processes that reduce ambient concentrations (e.g., burial, biodegradation, volatilization, photolysis, and dilution) are themselves first order processes. Because temporal trends are assumed to follow first order kinetics, temporal trends were tested with linear regression analysis after transforming concentrations to the natural logs. This produces the following equation

$$\ln(C_t) = \ln(C_0) + r * t$$

In which all parameters are the same as in the first equation. The existence of a first order decline

can then be tested, statistically, with linear regression of log concentration on time of collection. Logarithmic transformation of concentration also tended to normalize residuals, a requisite for the use of parametric statistics.

Because absolute changes in concentrations fall as concentrations fall, first order reactions will always trace a concave up path when plotted on the usual linear XY graph (Figure 1). The inevitable concave up shape, unfortunately, misleads many viewers into believing that concentrations of organochlorines (OCs) are stabilizing over time. Thus, all temporal trends will be depicted on the semilog scale. Time is plotted on the linear X-axis while untransformed concentrations are plotted on a logarithmic Y-axis (Figure 2). Readers unfamiliar with the semilog scale should be advised of the following. First, equal distances on the logarithmic Y-axis represent equal percentage changes in concentration. Consequently first order declines now trace a straight line (Figure 2), eliminating the optical illusion of stabilization that occurs on the linear XY plot. Secondly, absolute changes in concentration tend to look smaller than when plotted on the linear Y-axis, as shown in Figures 1 and 2. When assessing progress over time, therefore, it is important for the reader to look closely at the Y-axis.

Because percent declines per year are more accessible than first-order rate constants, rates of decline over time will be described in the text below in terms of percent declines as opposed to the first order rate constants produced by the regression analyses.

Results

Gull Eggs from the Great Lakes

The CWS eggs sampling program is the best available data base for determining status and trends of organochlorines in the Great Lakes. Since the early 1970s, CWS has assessed OC concentrations in gull eggs from a number of colonies across the Great Lakes. The positions of the colonies are depicted in Figure 3. The gull egg data are extensive over time and space and have benefited from a relatively consistent sampling and analytical methodology (described in Bishop et al. 1992 and Petit et al. 1994)¹⁰. Another advantage of the gull egg data is that the data are regularly disseminated and available to the Great Lakes research community. Thus, the strengths and limitations of these data are better understood than other Great Lakes data sets (e.g., see Smith 1995a, Hebert et al. 1996, Hebert et al. 1998).

These data were statistically analyzed (by colony and by Great Lake grouping) to determine whether trends were statistically significant. OCS in herring gull eggs declined significantly ($p < 0.05$) from 1987 to 1998 in eggs from all colonies except three – Leslie Spit (Toronto Harbor) and Snake Island on Lake Ontario, and Chantry Island on Lake Huron (Figure 4). In the latter three cases, the regressions were marginally significant (e.g., $p < 0.10$). Moreover, when the data from all colonies on a Great Lake were grouped together, rates of decline are highly significant for each Great Lake.

¹⁰ For complete reference citations see bibliography in Appendix V.

On average, OCS concentrations in gull eggs from colonies on Lakes Erie, Huron, and Ontario tended to be higher than those from Michigan and Superior (Figure 5), although there was considerable variability between colonies on the same Great Lake (Figure 6). OCS concentrations were only sometimes elevated in gull eggs taken from colonies near historical sources such as Channel Shelter Island on Saginaw Bay, the Fighting Island Colony on the Detroit River, and the colonies on Lake Ontario. On the other hand, OCS concentration from the Port Colborne colony on the eastern Basin of Lake Erie and the Niagara River colony were both quite low despite their proximity to historical sources in the Ashtabula and Niagara Rivers (Battelle 1998). The rates of OCS decline over time among lakes were remarkably consistent, despite intra-lake variability. By colony, rates of decline varied from about 9% per year at Channel Shelter Island to about 24% per year at Double Island (Figure 4), both on Lake Huron. However, the rates of decline were not significantly different (ANCOVA, $p > 0.05$) across all Great Lakes colonies, and all colonies tended to decline at an average rate of 18% per year. Concentrations of OCS in most colonies are approaching the detection limit (about 1 ppb) (Figures 5 and 6). Eggs were below the limit of detection at least once between 1995 and 1996 in all colonies except two – the Middle Island colony in Lake Erie and the Channel Shelter Island colony in Lake Huron.

Conclusion: From 1987 to 1998, concentrations of OCS in gull eggs fell significantly and somewhat rapidly, on average about 18% per year (Table 3). The rates of decline did not differ statistically among colonies, and declines were very uniform across lakes and connecting channels. These decreases have reduced the concentrations of many colonies to levels near the limit of detection. Spatially, colonies from Lakes Ontario, Erie, and Huron have similar concentrations. Concentrations of OCS in gull eggs from colonies on Lake Superior and Michigan are similar to each other but lower than from the other Lakes.

Spottail Shiners from the Niagara River and Lake Ontario.

Another very useful long-term database for OC in the Great Lakes is provided by spottail shiners represent These data are the property of the OMOE and the Canadian Government, and collection and analytical methods are described in Suns et al. (1982, 1993) and Suns and Hitchin (1992). As with the gull-egg data, the spottail-shiner data benefit from relatively consistent methods over the long term as well as frequent sampling over time and space. However, only the data from the Niagara River were obtainable for this report. OCS concentrations in spottail shiners from the upper Niagara River are only rarely above the detection limit, making temporal trends analyses impossible. However, OCS concentrations in shiners from the lower Niagara River were generally above the limit of detection in the beginning of the sampling period in the mid-1980. When less than detect values are assigned the value of 1/2 the detection limit, OCS concentrations in the lower Niagara River are estimated to have fallen about 8% per year ($p < 0.05$, Figure 7)¹¹.

¹¹ Because OCS data are limited and often below the limit of detection, values, usually 1/2 the detection limit, were assigned to concentrations that were below the limit of detection. This practice allowed use of the information contained in analyses that were below the detection limit and seemed a reasonable compromise between the two possible extremes of applying the detection limit or zero. The latter is also problematic because zero cannot be log-normalized.

Use of 1/2 the detection limit is only recommended for use with trends analyses and does not imply, nor should it be

Conclusions: Concentrations in shiners taken from the lower Niagara declined at about 8% per year, falling from about 4 ug/kg in the mid 1980s to less than detection in the mid 1990's.

Lake Trout from Lake Ontario

The Canadian Department of Fisheries and Oceans (F&O) collects lake trout and smelt from each of the Great Lakes on an annual basis. F&O data are not readily available to the public or Great Lakes scientific community, so the quality, methods, and extent of these data could not be ascertained. According to information presented in Huestis et al. (1996), lake trout samples from Lake Ontario are analyzed for OCS. These data show significant ($P < 0.05$) declines, about 10% per year, in OCS over time in Lake Ontario lake trout.

Conclusion. Concentrations of OCS fell significantly, about 10% per year, in Lake Ontario lake trout from 1977 to 1993.

Water and Suspended Sediments from the Niagara River

The Upstream/Downstream monitoring group samples water at the beginning and end of the Niagara River, at Fort Erie and Niagara-on-the-Lake. These data, therefore, provide information on water quality conditions in Lake Erie, the Niagara River, as well as information about loading of OCS to Lake Ontario. This is a high quality database with relatively consistent methods over time and very frequent sampling. These data are also regularly published and easily obtainable by the Great Lakes science community.

OCS data were obtained from the Upstream/Downstream sampling group for the period between 1989 and 1995. During this period, water samples were generally taken every week. Whole water samples were divided into aqueous and suspended sediments, and chemical analyses were conducted on these two fractions. Although there are MDLs reported for both fractions -- 0.05 ng/l for the aqueous fraction and 2.7 ng/g of suspended sediment -- concentrations well below the MDL (20% or less of the MDL) are routinely reported. Thus, these reports produce three types of data: estimated concentrations above the MDL, estimated concentrations below the MDL, and data listed as below the detection limit.

At Fort Erie, at the origin of the Niagara River, 281 aqueous fractions and 285 sediment fractions were analysed¹². None had a reportable concentration of OCS. Thus, OCS was never detected in 566 analyses representing about 285 water samples. OCS was detected at the mouth of the Niagara River at Niagara-on-the-Lake. For the aqueous fraction, 270 analyses were conducted.

inferred to mean, that the actual concentrations are really 1/2 the detection limit. The practice should not be used as an indication of substance presence or for purposes of source identification. In many cases (e.g., with suspended sediment concentrations in the Niagara River and with bottom sediments), actual concentrations are probably considerably less than 1/2 the detection limit.

¹² The number of aqueous data points does not equal the number of suspended sediment data point because data for one or the other medium are sometimes, albeit infrequently, rejected because of QA problems.

Concentrations for the aqueous fraction were 43 times between 1989 and 1991, but not since then. For the adsorbed fraction, reportable concentrations of OCS were detected more frequently concentrations, about 55% of the time. To determine long-term trends, total water concentration of OCS for each sample was estimated in the following manner

$$[\text{OCS}]_{\text{total water}} = [\text{OCS}]_{\text{aqueous}} + [\text{OCS}]_{\text{adsorbed}} * [\text{suspended solids}].$$

Given the large number of analyses below detection, the results of a trends analysis will depend somewhat upon what values are given to unreported values. To insure that trends were real, various values were given to the unreported values for adsorbed OCS: 1/2 the detection limit (1.35 ng/g), 1.0 ng/g, and 0.37 ng/g, the lowest value reported. OCS was rarely reported in the aqueous fraction, so unreported data in the aqueous fraction were set equal to zero.

No matter how non-reported values were treated, OCS concentrations were estimated to have fallen significantly over the period. However, the estimated rate of decrease was dependent upon what values were used for unreported values. OCS concentrations declined by about 40% per year when unreported values were set equal to 0.37 ng/l, but only about 28% per year when unreported values were set equal to 1.35 ng/g, one half the detection limit (Figure 8). Ignoring the aqueous fraction and setting unreported values equal to 1.35 ng/g, OCS concentrations on suspended sediments fell about 21% per year. These analyses demonstrate that OCS concentrations really did decline over this period. However, detecting future declines will become more difficult as more and more analyses yield non detect values.

All of these measured rates of decline are probably faster than the long-term average. Oliver and Charlton (1988) measured OCS in the Niagara River several times in the fall of 1982. They found an average OCS concentration of 0.06 ng/l in whole water, which is approximately three times the geometric mean concentrations found in 1989. These two dates trace a 15% per year decline. Similarly, OCS concentrations in the Niagara Bar (discussed below) demonstrate long-term declines of about 14.5% per year.

Conclusion. From 1987 to 1995, OCS concentrations at Fort Erie were always lower than the detection limit in both water and suspended sediments. At Niagara-on-the-Lake at the mouth of the Niagara River, OCS was detected at reportable concentrations on a semi-regular basis, especially adsorbed to suspended sediments. OCS concentrations in whole water and suspended sediments fell rapidly over this period, between 21% to 40% per year, depending upon the value applied to unreported values. Based on these data, loading of OCS to Lake Ontario is estimated to have decreased about 70% or more between 1989 and 1995.

Suspended sediments and water from the St. Clair River

MOE monitors water at two points in the St. Clair River, Port Edward at the beginning of the of the St. Clair River and downstream at Port Lambton. The methods are similar to those used in the Upstream/Downstream sampling: sampling on a frequent basis (every two to three weeks), fractionation into an aqueous and sediment fraction, detection limits of 0.05 ng/l and 2.7 ng/g, respectively, and analysts who routinely report concentrations below the detection limit. Of 103

analyses of the aqueous fraction sampled at Port Edward between 1987 and 1996, only 5 samples had reportable concentrations of OCS. These 5 samples averaged 0.02 ng/l OCS. Only two of 111 analyses of suspended sediments had reportable concentrations of OCS.

Reportable concentrations were more frequent downstream at Port Lambton. Of 141 analyses of the aqueous fraction taken between 1987 and 1994, only 7 had reportable concentrations of OCS. However, OCS was regularly reported adsorbed to particles. About 90% of analyses of suspended sediment yielded reportable concentrations of OCS (Figure 9). When unreported concentrations are set equal to one half the detection limit, these data produce a significant decline of about 15% per year.

Conclusions: OCS concentrations have generally not been detected at Port Edward at the origin of the St. Clair River. Downstream at Port Lambton, OCS concentrations dissolved in water are also infrequently detected above the detection limit. However, concentrations adsorbed to suspended sediments are generally at reportable concentrations, although these concentrations appear to be falling at about 15% per year over the last decade.

Data for the St. Lawrence River/Outflow from Lake Ontario

Environment Canada also samples OCS at the origin of the St. Lawrence River. These data are diagnostic of St. Lawrence conditions as well as Lake Ontario. The data are apparently generated using the same general methods as with Niagara River and St. Clair River sampling. Reported detection limits were 0.07 ng/l for water and 2.7 ng/g for the adsorbed fraction. For 85 samples taken from 1989 to 1994, OCS concentrations were reported once in the water column and 11 times in the suspended sediment fraction. All of the reported concentrations were below the detection limits. The eleven concentrations reported for the sediment fraction averaged 0.9 ng/g. The single value reported for the aqueous fraction was 0.01 ng/l, which is 1/7th the MDL¹³.

Conclusion. Concentrations of OCS in the headwaters of the St. Lawrence River/outflow of Lake Ontario are infrequently detected at concentrations that can be estimated. Current concentrations are well below the detection limit.

Bottom Sediments from Lake Ontario

Two sediment core samples have been taken from Lake Ontario and analyzed for OCS. Durham and Oliver (1983) took a sediment core in the Niagara Bar in 1981, and core samples from the Niagara Bar were taken in 1995 by New York Department of Environmental Conservation (NYDEC 1996). The two cores showed a consistent pattern (Figure 9). In both cores, OCS concentrations in sediments apparently peaked about 1960 and then declined at about 13.5% per year (Figure 10). For the NYDEC sample, OCS concentrations in sediments deposited after about 1981 were always below the detection limit, which ranged from about 13 to 6.4 ug/kg.

¹³ As these data are below the MDL, they represent samples for which OCS is probably present extremely low levels, but the exact magnitude is unknown.

The yearly declines estimated between 1960 and 1981, when OCS concentrations were above the detection limit, can be extrapolated to the present. Assuming that past rates of decline continued to the present, OCS concentrations in Niagara Bay sediments in the early 1990s should be between 0.5 and 1.0 ug/kg (Figure 8). This projection can be compared to the sediment trap data from the Niagara Bar (Oliver and Charlton 1988) and suspended sediment data from the Upstream Downstream Monitoring of the Niagara River (see section above on the Water Concentrations in the Niagara River). Sediments captured in sediment traps should reflect sediments being laid down during that period. Similarly, OCS concentrations in sediments deposited in the Niagara Bar should be a function of OCS concentrations on suspended sediments at the mouth of the Niagara River, which is the source of most particles settling onto the Niagara Bar.

In both cases, however, concentrations of settling and suspended sediment must be normalized to organic carbon levels similar to those found in bottom sediments to reflect the reduced binding capacity of coarser, less organic sediments that finally settle onto the Niagara Bar. Most recently deposited Niagara Bar sediments are about 3.1% organic carbon (NYDEC 1996). Organic carbon concentrations found in sediment traps were about twice those found in settled sediments (Oliver and Charlton 1988). Thus, sediment trap concentrations were divided by two to normalize for organic carbon (Figure 10). The concentrations measured by Oliver and Charlton fall very near the extrapolation line.

The fraction of organic carbon in Niagara River suspended sediments varies considerably, ranging between about 5% to over 30% organic carbon (Kuntz 1988)¹⁴. Assuming a geometric mean concentration of 10% would require a correction factor of 3.2 to normalize the suspended sediment to the 3.1% organic carbon of the sediments deposited in the Niagara Bar. When concentrations of OCS on suspended sediments from the mouth of the Niagara River are divided by this correction factor, most recent suspended sediment concentrations also fit right on the extrapolation line (Figure 10). This combination of information suggests that OCS loading to Lake Ontario has continued to fall at about the same rate (about 14.5% per year) from 1960 to the present.

Conclusion: As evidenced by OCS concentrations in Niagara Bar sediments, loading of OCS to Lake Ontario apparently peaked in the early 1960s, and has fallen about 14.5 % per year since that time to the early 1980s, after which concentrations became too low to be detected. More recent data on settling particles in the Niagara Bar region and suspended sediments in the Niagara River have concentrations similar to those extrapolated from the long-term trends, suggesting that this rate of decline has continued to the present.

Additional Data on Status and Trends. OCS was measured in Lake Ontario water column twice, in 1984 (Oliver and Niimi 1988) and 1996 (EPA, unpublished data). Both samples were taken during spring overturn in open water areas of the Lake and were replicated at several sampling locations. Oliver and Niimi report a mean OCS concentration of 4.7 pg/l in the aqueous phase. For the 1996 EPA sampling, all samples yielded concentrations below the detection limit:

¹⁴ These data were kindly supplied by J. Merriman, Ecosystem Health Division of the MOE.

roughly 0.5 pg/l in the aqueous phase and 0.2 pg/l in the adsorbed phase. As OCS was not detected in any of the 4 samples (three stations with one station duplicated), it can be assumed that the real OCS concentration was well below the detection limit. Assuming that the concentration was ½ the detection limits, or about 0.25 pg/l. Using these two dates only, there was about a 95% decrease in water column concentrations of OCS, or about 22% per year. This observation should be treated with caution. Only two periods were sampled, and the analyses were conducted by different analysts.

Discussion.

The above analysis was limited to straightforward description of observable status and trends of OCS in Great Lakes media. These analyses addressed basic questions of how OCS concentrations have varied in time and space. In the context of the “virtual elimination strategy”, there is also the less straightforward question of what spatial and temporal trends really mean. Specifically, can spatial and temporal trends in measured concentrations be used as an indicator of underlying trends in external loading?

The simple answer to this question is “no.” The problem with inferring changes in loading from changes in ambient concentrations is twofold. First, measured concentrations in many media are often not good indicators of in-lake inventories, especially when measurements are limited. Second, for systems at non-steady-state with external loading, trends of in-lake inventories may be based largely upon internal fate processes and have little or nothing to do with trends in external loading (Endicott et al. 1992a,b, Smith, under review.) With respect to the first problem, concentrations of organochlorines in biota (lake trout, gull eggs, spottail shiners) are known to respond to a number of other factors in addition to abiotic concentrations and levels of external loading. These factors, which confound interpretation of observed trends, include winter weather, prey availability, aquatic prey chain length and structure, terrestrial vs. aquatic foraging, limnological factors, and potential effects of inter-lake migration (Rasmussen et al. 1990, Rowan and Rasmussen 1992; Smith 1995a,b, under review; Hebert et al. 1995; 1998) Concentrations of chemicals in the water column and sediments are confounded by sampling error and actual variability due to storms and mixing events as well as long-term changes in lake trophy and suspended sediments concentrations.

In view of the confounding factors affecting organochlorine concentrations, caution should be exercised when extrapolating observed trends, over time and space, in any of the media above to underlying trends in in-lake inventories, and from there, to trends in external loading. This is especially true of inferences based on small data sets and short time trends. For example, consider the OCS data for gull eggs from Lake Ontario (Figure 11). The long-term trend from 1987 to 1998, which shows a significant decrease in OCS concentrations over time, actually consists of three short-term trends: concentrations tended to remain constant from 1987 to 1993, fell precipitously, about 90%, from 1993 to 1995, and then rebounded somewhat from 1995 to 1998 (Figure 11).

Several factors suggest that none of these short-term trends is responding to underlying changes of in-lake inventories levels or external loading of OCS. For example, the initial period of stable

concentration is more likely attributable to one of the confounding factors affecting organochlorine concentrations in gull eggs (e.g., food chain effects and/or the weather effect). This is apparent because most of the organochlorines also show stable concentrations from the period 1987 to 1993 (Smith 1995a). The organochlorines have disparate sources of external loading to Lake Ontario, and it is not reasonable to expect that the loading of the different external sources of different organochlorines would be synchronized. The short-term pattern of stable OCS concentrations in gull eggs is also inconsistent with data from Niagara River loading. The Niagara River should be the primary external source of OCS to Lake Ontario. Loading of OCS from the Niagara River declined rapidly, from 70% to 80% at the same time that gull egg concentrations remained constant (Figure 8 vs. Figure 11). With respect to the precipitous decline of OCS concentrations from 1993 to 1995, it is highly unlikely for OCS inventories in Lake Ontario to fall much more than 10% per year, even under condition of complete zero loading (e.g., see Endicott et al. 1992a).

On the other hand, more reliable indicators of trends in ecosystem inventories, but not necessarily external loading, can be obtained by focussing on long-term trends and by looking for similar trends among different media. Despite potential problems with any one data set, there is a high degree of certainty that OCS concentrations have really been falling over the period from 1980 to at least the mid-1990s in Lake Ontario. As summarized in Table 3, there are statistically significant and quantitatively substantial declines in all of the following media:

- inflowing Niagara River water concentrations (1989 to 1994)
- spottail shiners residing in that inflowing water
- in-lake water column concentrations (1994 to 1996, two dates only)
- gull eggs (1987 to 1998)
- lake trout (1977-1993)
- in-lake sediments (1960 to 1981 or 1994 if suspended sediment data can be included).

Similarly, we can be reasonably certain that OCS concentrations in the St. Clair River/Detroit River are also actually declining, because OCS concentrations are declining in the water column and in gull eggs. Data on temporal trends in other Great Lakes areas are mostly limited to gull eggs. This might be problematic, except that OCS levels are falling at all of these other colonies, suggesting that OCS inventories are indeed declining in the Great Lakes. Equally important, Lake Ontario and the St. Clair/Detroit River are two of the three areas in which OCS levels are elevated. With the exception of Saginaw Bay, where OCS is also elevated in gull eggs, temporal trends in other Great Lakes areas are of less importance because levels in most media are already near or at the detection limit.

Keeping in mind the limitations of the data, the following addresses the questions posed at the beginning of this discussion.

- **What are current levels of OCS in Great Lakes media?**

As shown in Table 3, current levels of OCS in most media are now at the limit of detection or rapidly approaching this limit at most sites in the Great Lakes. The notable exceptions to this are

OCS concentrations in lake trout in Lake Ontario. Extrapolating past rates of decline (about 10% per year) onto early 1990's concentrations (about 30 ug/kg in whole raw lake trout) suggest that whole raw lake trout will continue to exceed the current detection limit (1ppb) till about 2025. It is also likely that OCS is above the detection limit in fish from the other Great Lakes, and potentially the St. Clair/Detroit River and Niagara River. Assuming a relatively constant relationship between gull eggs and fish, it is likely that OCS would be about as high in Lake Erie and Lake Huron fish as in Lake Ontario. OCS might also be detectable in very large lake trout from Lake Superior and Lake Michigan.

- **How have levels changed over time?**

In all media with adequate data, levels of OCS are decreasing significantly and, compared to other organochlorines, relatively rapidly, e.g., 8% to 30% per year (Table 3). Rates of decrease over time are generally highly statistically significant, quantitatively substantial, and consistent across media, time, and space. It can be concluded with a high degree of certainty that OCS concentrations in the Great Lakes have declined dramatically over the last two decades.

- **How do concentrations vary over space, i.e., from place to place?**

Gull egg data suggest that OCS burdens in Lake Huron, Lake Erie, and Lake Ontario are higher than in Lakes Superior and Michigan, although there is substantial intra-lake variability between colonies from Lake Erie and Huron. Elevated concentrations appear to be related to historical sources in Saginaw Bay, the St. Clair River, and Lake Ontario. Data from other media are limited, but tend to support the spatial trends found in gull eggs.

- **What can be deduced concerning current sources and future trends?**

The available data suggest that atmospheric sources were probably never an important source of OCS to Great Lakes ecosystems. Gull eggs colonies with elevated concentrations are generally downstream of historical sources of OCS in Saginaw Bay, the St. Clair River, and the Niagara River. Concentrations of OCS in gull eggs from colonies on Lake Michigan and Lake Superior, which are far away from historical sources, tend to be about 3 to 4 times lower than those downstream of suspected historical sources. It is also important to note that concentrations of OCS in gull eggs from all of the colonies are falling at about the same rate in all Lake groupings (Figure 5). This observation is inconsistent with the hypothesis of significant current atmospheric inputs, as one would expect atmospheric dependent sites to decline at a different rate than colonies primarily affected by past and current riverine and point sources. The rapid decreases in OCS concentration in gull eggs and the other media also suggest that current atmospheric loading is relatively insignificant and allows unimpeded declines of OCS in the lakes. Consistent with all of these observations, OCS is rarely if ever detected in air monitoring near the Great Lakes (Dann 1997).

If atmospheric loading of OCS can be assumed to be negligible, that leaves current external loading from point and non-point sources and internal loading from sediment inventories due to past external loading. It is critical to differentiate between internal and external loading. External

sources are generally controllable and likely to yield some benefits if controlled. Sediment inventories, on the other hand, are not readily easily controlled and yield less certain benefits as they will remediate naturally, albeit slowly, without further action.

The two different sources should produce different patterns over time and space. Systems whose OCS concentrations are tightly controlled by external sources should have very site specific and unique temporal patterns, because external source control will be a site-specific function of regulatory commitment, local economic conditions, amenability to control, and other site specific factors. Thus, if, as is often hypothesized, sites on the Niagara River are a major current source of OCS to the Lake Ontario, one would expect declines in OCS in the Niagara River and Lake Ontario media to be episodic and tied tightly to specific remediation activity. It is also expected that the temporal patterns of decline will be very different from OCS declines at other sites, and very different from declines of other chemicals (e.g. PCBs and DDE) not associated with sources of OCS.

The patterns of decline for systems controlled by internal sediment stores are likely to be very different from those controlled by current external sources. As the fate processes controlling declines in sediments are relatively constant across time and space and across PTS chemicals, one would expect systems controlled by internal inventories to decline at fairly similar rates through time, across lakes, and among persistent toxic chemicals. The data, while limited, seem more consistent with the latter hypothesis. The very similar declines of OCS in the gull eggs across colonies suggests some common mechanism of decline (potentially, for example, fate processes affecting sediment inventories.)

Great Lakes system dominated by internal sediment inventories should also have orderly declines of different persistent toxic substance. That is, concentrations of different organochlorines should decline in a predictable fashion based on the vulnerability to fate processes affecting concentrations in the sediments. More volatile and degradable chemicals like hexachlorobenzene should dissipate faster from the Great Lakes than more stable, less volatile chemicals such as Mirex and dieldrin. PCBs are of intermediate vulnerability to various fate processes and should dissipate with an intermediate speed. The predicted rates of relative decline for internal inventories of various organochlorine can be estimated from the model of Endicott et al. (1992a) under a condition in which external loading was reduced to zero. In this case, long-term declines of these chemicals depends on vulnerability to various loss processes. These estimated zero-loading declines can be compared to yearly declines observed for lake trout in Lake Ontario (Huestis et al. 1986). As can be seen from Figure 12, there is a significant relationship between predicted and observed declines of different organochlorines in Lake Ontario lake trout (regression analysis, $p < 0.05$). That is, as predicted, the different organochlorine are declining in a significantly orderly process based on their vulnerability to internal fate processes. This significant relationship further supports the hypothesis that external loading is unimportant. It is also important to note that OCS is actually declining faster than predicted. At the least, this graph demonstrates that OCS, which has received little regulatory attention in the last several decades, is declining considerably faster than compounds like DDT, PCBs, and TCDD, which have received much regulatory attention and have been under very strict regulation. This observation is inconsistent with a system dominated by external sources, which ought to be more controllable

than internal sediment inventories.

There are other data to substantiate that current concentrations of OCS in Lake Ontario are based on internal sediment inventories as opposed to current external loading. Loading from the Niagara River can be estimated from the Upstream/Downstream monitoring. Best estimates of early 1990s loading from the Niagara River are about 4.3 to 6 grams per day, depending upon what values are assigned to non-detection data. According to Endicott et al, model, this loading of OCS should produce lake trout concentrations of about 5.2 to 3.8 ug/kg in whole lake trout. These predicted values are 6 to 8 times lower than observed concentrations for this period, about 31 ug/kg (Huestis et al. 1996). The discrepancy between observed and predicted concentrations also supports the hypothesis that OCS concentrations in Lake Ontario are largely due to internal sediment inventories, as opposed to current external loading.

Table 3. Summary of results. Decreases are based on regression analyses. ND means not detected. NA means not applicable; some data sets had insufficient frequency of detected concentrations to permit trends analyses.

Medium	Location	Time Frame	Decrease (% per year)	Most recent conc.
Gull egg	Lake Ontario	1987-1998	Yes (17%)	Some ND
Gull egg	Lake Erie	1987-1998	Yes (16%)	Some ND
Gull egg	Lake Huron	1987-1998	Yes (16%)	Some ND
Gull egg	Lake Superior	1987-1998	Yes (17%)	Some ND
Gull egg	Lake Michigan	1987-1998	Yes (20%)	Some ND
Gull egg	Niagara River	1987-1998	Yes (17%)	Some ND
Gull egg	Detroit River	1987-1998	Yes (20%)	Some ND
Spottail Shiner	Lower Niagara River	1985 -1995	Yes (8%)	100% ND
Lake Trout	Lake Ontario	1977-1993	Yes (10%)	0 % ND
Water	Niagara River	1989-1995	Yes (16%-21%)	50% ND
Water	Upper Niagara River	1989-1994	NA	100% ND
Water	Lake Ontario	1984, 1996	Yes (20%)	100% ND
Water	St. Clair River (Port Edward)	1989-1996	Yes (15%)	>95% ND
Water	St. Clair River (Port Lambton)	1989-1995	NA	10% ND
Water	St. Lawrence	1989-1996	NA	90% ND
Bottom Sediments	Lake Ontario	1960-1981 (95)	Yes (12%)	100% ND

A Critical Review of the Battelle Report

OCS Formation Considerations

Mr. Larry LaFleur, a National Council of the Paper Industry for Air and Stream Improvement Fellow, has studied the mechanism of formation of chlorinated phenolic compounds, especially PCDD/Fs, extensively. He has reviewed the second Battelle report and has concluded that from a mechanistic and sound scientific process standpoint, the document is seriously flawed. His observations include the following.

I. Introduction

A fundamental premise of modern synthetic chemistry is that one needs to understand the basic reaction mechanism before one can reliably predict products. Even if one knows the proper mechanism, the appropriate reaction conditions (e.g., temperature, catalyst, sufficient time, proper solvents, suitable concentrations, etc.) must be present in order for the reaction to proceed. Many reactions which occur in one solvent, such as free radical chlorination in aprotic solvents, would be suppressed in a protic solvent such as water. Finally, the necessary starting materials must not only be present, but must be present in proportions conducive to the reaction. In many respects, synthetic chemistry is the science of successfully optimizing the various combinations of these variables to achieve a specific, desired outcome.

Accordingly, any technically creditable extrapolation from known sources of octachlorostyrene (OCS) to potential other sources requires a careful consideration of reaction mechanisms, conditions, and stoichiometry. Thus, sufficient evidence that each of these criteria have been met must be demonstrated before one would have sufficient cause to further examine a hypothesized new source.

In Sections II, III, and IV, we discuss mechanistic considerations, reaction conditions, and stoichiometry of some known sources of OCS. In this discussion, we highlight the types of corroborating data that would be necessary to extrapolate known OCS sources to other sources. In Section V, we give several examples of how a more critical consideration of these fundamental principles would show that there are no data to support the hypothesis that these processes are potential sources of OCS. In Section VI, we briefly discuss the Battelle approach to estimating an OCS inventory based on the EPA dioxin inventory and show that the underlying assumptions are fundamentally flawed.

II. Mechanistic Considerations

A. Hexachlorobenzene, octachlorostyrene, and PCDD/F

The Battelle report notes an apparent relationship between hexachlorobenzene and octachlorostyrene where PCDD/F have also been reported. These different mechanisms seem to arise where the starting materials and/or conditions are such that hexachlorobenzene can be

formed. Apparently, under these same conditions hexachlorobenzene can further react to form octachlorostyrene or it can proceed through a different series of reactions to form PCDD/F. Under these circumstances, there is an apparent relationship between octachlorostyrene and PCDD/F. However, it would be inappropriate to conclude that the reverse would also be true. If PCDD/F are formed by some other mechanism under other conditions, it may or may not coincidentally produce either hexachlorobenzene or octachlorostyrene. As is discussed in Section V, there are several examples of PCDD/F formation where there is no reason to suspect formation of octachlorostyrene.

B. The *de novo* synthesis hypothesis

In the review of sources commissioned by EPA in 1985, Schulman and Klingele¹⁵ discussed theoretical mechanisms for octachlorostyrene formation. They proposed the following hypothesis:

“Each reaction in the stepwise formation of PCSs could fall into one of two broad categories:

1. ultratrace concentrations of reactants combine in high yield; or
2. high concentrations of reactants combine in ultratrace yields

In the former case, the free energy of formation of the product at each step is lower than the free energies of reactants and other competing products. In the latter case, the free energies of formation of reactants and other products are lower than the PCS precursor products, but the statistics of the reaction chemistry assure that some of each of the successive precursor products will be generated in some amounts.

Reaction conditions favoring the former case would probably involve high energy environments where polychlorinated aromatics like PCSs would be stable relative to other molecular configurations. Such conditions would be likely to prevail in high energy electro-, pyro-, photo- and thermochemical reaction environments. Reaction conditions favoring the latter case would involve lower energy reactions in which polychlorinated organic substances are reactants or intended products. Further, if PCSs were removed from the reaction environment fastest than other, more stable products, say via physical processes such as sorption to the walls or bottom of a reactor vessel or to particulate matter in the reaction matrix, significant quantities of PCSs could still be generated, even though not thermochemically favored.”

Schulman and Klingele (1985) went on to propose a theoretical mechanism that might lead to the formation of octachlorostyrene through a series of high energy free radical chlorinations and polychloro alkyne radical coupling reactions. This mechanism is termed the *de novo* synthesis mechanism. This mechanism was not proposed based on any experimental investigations on their part, but was instead based on their review of potentially relevant published literature and their interpretations.

¹⁵ For complete description of references see bibliography contained in Appendix VII.

Their final conclusions based on their deliberations were:

“Whenever a carbon source is exposed to chlorine and large energy flux, as either electricity or heat, and indicator compounds such as carbon tetrachloride, perchloroethylene, and perchlorobenzene are produced, PCS is a suspected byproduct. Whenever aromatic compounds, particularly chlorinated ones, are exposed to conditions where chloroalkyl radicals may be present, PCS is a suspected byproduct.”

We would add to those observations the fact that the chemistries used to support their hypothesis were free radical reactions occurring under extremely high energy conditions, and were often conducted with a very large excess of chlorine (relative to the available carbon). We believe these are important distinctions.

The Battelle report cites this hypothesis, describes it generally, but does nothing to further advance it or support it with new information.

Based on the rationalizations used to advance this hypothesis, the *de novo* mechanism is clearly a high energy free radical chlorination and coupling mechanism. In order to invoke this mechanism for a potential new source of OCS, one should provide supporting data to justify the hypothesis. As discussed in the Schulman and Klingele report, one should provide evidence of other intermediates or by-products that support that a similar mechanism is operative. These may include carbon tetrachloride, various tri- and tetra- chloro ethanes and ethylenes, hexachlorobutadiene, di-, tri-, tetra-, penta-, and hexachloro- benzenes, etc. Since many of these are actual commercial products, it would be necessary that more than just a single intermediate be identified to support the like mechanism argument.

C. Magnesium and nickel refining

In one reference, the Battelle report states that there are indications of formation of both OCS and PCDD/F (Ohme et al. 1989) in magnesium and nickel refining. The authors also note that the processes result in the formation of hexachlorobenzene. Ohme et al. describe a unique PCDD/F fingerprint where the PCDF to PCDD ratio is 50:1. This would indicate that it is appropriate to suggest formation of OCS from a source if, and only if, the hexachlorobenzene was demonstrated to be present and the PCDF to PCDD ration was approximately 50:1. A more detailed examination of the PCDD/F fingerprint reported by Ohme et al. (1989) should be performed, and additional criteria should be considered (e.g., the 1,2,3,7,8-PeCDD to 2,3,7,8-TCDD ratio was 11:1). These criteria would provide a technical justification for assuming a like mechanism might be operative. At the same time, it should also be pointed out that the Ohme et al. work explicitly pointed out the vast differences between the Mg and Ni refining PCDD/F fingerprint and the fingerprint typically observed in incineration sources. This is explicit evidence that there is a completely different mechanism than the one responsible for the OCS from Mg and Ni refining that may be operative in incineration sources.

D. Other metal refining processes

Doring et al. (1992) describe the concurrent formation of OCS, HCB, pentachlorobenzene

(PeCB), decachlorobiphenyl (DCB), and PCDD/F from a copper smelting process. Doring et al. (1992) describe conditions necessary for the formation of these compounds as follows:

“A chlorine source is present (sodium chloride) and the reductive conditions transform Cl^- to Cl^\cdot -radicals. These are then able to chlorinate the aromatics formed by radical processes from the carbon source (coal) at the high process temperature.”

They later note:

“The chlorination roasting process of the copper slag has some similarities with the production of waterfree magnesium chloride (reductive conditions at high temperature ($>700^\circ\text{C}$), presence of carbon and Cl^\cdot -radicals).”

Much like the fingerprint for the above described Mg process, there is a clear predominance of PCDFs, with the PCDF/PCDD ratio at about 10:1.

This illustrates the importance of corroborating mechanistic hypotheses with confirmatory data. Only when clearly analogous conditions are observed and similar fingerprints are demonstrated (e.g., PCDF/PCDD ratio of 10:1, presence of HCB, DCB, and PeCB) can one reasonably infer the formation of OCS.

E. Perchloro solvent manufacturing

In the work reported by Pereira et al. (1988), which the Battelle report cites as evidence of a link between OCS and HCB, the authors also report the presence of high levels of di-, tri-, tetra-, and penta-chlorobenzenes, as well as hexachloro-1,3-butadiene and octachloronaphthalene as by-products of chlorinated solvent manufacturing. Thus, before invoking an argument that the presence of HCB is an indication of potential OCS via the same mechanism, evidence of these other co-contaminants that would support the hypothesis of a like formation mechanism should be provided. Otherwise, there is no justification for supposing a like mechanism.

To summarize, before any surrogate chemicals like PCDD/F or HCB can be used as indications of the potential for OCS formation, there should be some corroborative data which provides supporting evidence that a like reaction mechanism is operative. Without such evidence, the extrapolation from one source to others using the presence of these proposed indicator compounds is technically insupportable.

F. Chlor-alkali production

The Battelle report sites the work of Kaminsky and Hites (1984) as evidence of the formation of OCS in the chlor-alkali process where carbon electrodes are utilized. In work published by Rappe et al. (1990), a PCDD/F fingerprint for this type of process was shown to produce a large predominance of PCDFs. For instance, sludge from electrodes was found to contain 52,000 pg/g 2,3,7,8-TCDF vs. non-detectable levels of 2,3,7,8-TCDD. Similar high ratios were found for the higher homologues. Thus, inferring a relationship between known sources of PCDD/F from electrolytic processes and the potential for production of OCS would only be technically defensible if it were demonstrated that the PCDFs clearly dominated the fingerprint. If another

fingerprint is observed, it would be sufficient evidence that an alternative mechanism is operative and that, in the absence of other evidence concerning that mechanism and its by-products, it would be inappropriate to infer the formation of OCS.

III. Reaction Conditions

Table 4 provides a partial summary of conditions where OCS has been demonstrated to form (as described in the Battelle report, not independently verified). All can be characterized as high energy processes. Some involve high electrical currents, some high temperatures, and some both. In many cases, Cl₂ gas or other chlorinated solvents are used to create certain atmospheres, and conditions are such that they are clearly intended to react. Characterization of other potential sources of OCS should include careful comparison of the conditions known to produce OCS and those of the candidate process.

Table 4. Reaction Conditions of Known Sources of Octachlorostyrene

Process	Temperature	Energy Input	Carbon Source	Chlorine Source
Chlor-alkali	not specified	electric current	carbon electrodes	brine and Cl ₂ produced
Mg refining	1000-1200°C	electrodes	carbon electrodes	Cl ₂ atmosphere
Al degassing	600°C	unspecified, (sufficient to melt Al metal)	hexachloroethane	hexachloroethane or Cl ₂
Cu smelting	700°C	unspecified, (sufficient to melt Cu metal)	coal	8% NaCl under reducing conditions
Secondary Pb smelting	1260°C	incineration	battery casings	PVC separators

IV. Stoichiometry

Examination of the metals refining processes described in the Battelle report strongly indicates that in most cases there is excess chlorine relative to carbon (high chlorine to carbon ratio). This is also true for the production of carbon tetrachloride and tetrachloroethane. If one considers the chlor-alkali process, where a large volume of Cl₂ is produced from a comparatively small mass of carbon (in the form of the electrodes), there is also a high Cl/C ratio. Under these circumstances, it seems apparent that the potential for the formation of highly chlorinated compounds like OCS exists. However, it would not be appropriate to assume that if the right temperature and/or other conditions were present, the same potential for formation of OCS exists where the ratio is the opposite.

To a certain extent, dilution may also be an important consideration. Reactions that proceed in high yield at high concentrations may not proceed at all if performed under dilute conditions.

V. Examples of the Use of These Principles

A. Pulp bleaching

A perfect example of the need to provide some supportive evidence of like mechanisms is the insupportable extrapolation of the historical presence of PCDD/F in pulp mill effluents and the suggested formation of OCS. It has been well established that the formation of PCDD/F in pulp bleaching was caused by electrophilic aromatic substitution of the unchlorinated dibenzo-p-dioxin and dibenzofuran (Kringstad et al. 1988; Voss et al. 1988; Berry et al. 1989; LaFleur et al. 1990).

This type of ionic chemistry occurs because bleaching is performed in an aqueous environment. Free radical chemistry (as invoked by the Schulman and Klingele *de novo* formation hypothesis) is detrimental to the quality of the pulp; thus, steps are taken to suppress this chemistry. In older bleaching processes, this involved the use of 12 to 15% chlorine dioxide, a free radical scavenger.

The active chlorinating agent responsible for the formation of PCDD/F in pulp bleaching is Cl_2 . In order to eliminate the potential formation of PCDD/F in bleaching, the US and Canadian pulp and paper industry has moved to the use of chlorine dioxide bleaching processes. The switch to this bleaching chemistry has virtually eliminated all TCDD/F formation, and forms the basis of the NPDES effluent guideline limitation recently promulgated by EPA.

EPA conducted extensive sampling and monitoring of a variety of bleaching processes in the development of their effluent guideline (Federal Register 1998; US EPA 1993). This work included testing for many of the compounds that would provide evidence for other potential OCS mechanisms. Included in these analyses were carbon tetrachloride; tri- and tetra-chloro ethanes and ethylenes; di-, tri-, and hexachlorobenzenes; hexachlorobutadiene; and even styrene itself. EPA found no evidence of the presence of these compounds in the bleach plants they studied. This provides further evidence that the types of high energy free radical chemistry required to form OCS are simply not present in pulp bleaching.

To summarize:

The historical formation of PCDD/F in the bleaching process has been demonstrated to be due to an electrophilic aromatic substitution mechanism, not a high energy free radical mechanism.

Since free radical chemistry has undesirable effects on pulp quality, steps are taken to minimize it.

The pulp industry has changed its bleaching practices to the point where TCDD/F formation is virtually eliminated. These process changes have significantly reduced the incidental formation of other chlorinated organics as well.

EPA's data generated during their development of the pulp and paper industry effluent guideline demonstrate the absence of other indicator compounds that should be present if the *de novo* OCS mechanism was operative.

Taken together, there is no justification for extrapolating from the historical presence of PCDD/F

in pulp bleaching to the potential for this process to produce OCS. In fact, the clear understanding of the reaction mechanisms responsible for the presence of PCDD/F in historical bleaching processes is evidence that OCS would not be expected.

B. Vapor phase degreasing

The Battelle report seems to liken the process of vapor phase degreasing with aluminum degassing. In the case of the aluminum degassing process, the temperatures are above the melting point of aluminum (reported by Battelle as 600°C), and either hexachloroethane or chlorine gas are introduced to force their reaction with hydrogen. Comparing this with solid metal parts at or just below the boiling point of the solvent (e.g., 74°C for 1,1,1-trichloroethane) and inferring a potential for the formation of OCS is not technically sound.

C. Pesticide manufacture

The Battelle report sites pesticide manufacturing as a potential source of OCS. The discussion seems to involve mostly 2,4-dichlorophenol and products made using it as an intermediate. The process cited in the Battelle report is the controlled chlorination of phenol using a reasonably selective chlorination agent. There is nothing in this process that even begins to suggest the kinds of conditions necessary to produce OCS.

The authors state, “The methods for producing 2,4-dichlorophenol include the direct chlorination of phenol and/or monochlorinated phenol using chlorine or sulfuryl chloride (SO_2Cl_2) with chlorination promoters and stabilizers. In as much as this reaction is known to form CDD/CDFs, it is by analogy, suspected of forming OCS,” citing Kirk-Othmer 1996. We have examined the Third Edition of the reference (which is the only edition we had ready access to), and find that the statement that “In as much as this reaction is known to produce CDD/CDFs...” is a very misleading interpretation. Kirk-Othmer noted that polychlorophenols are starting materials for the synthesis of PCDDs and use 2,4,5-trichlorophenol as the starting material for 2,3,7,8-TCDD. There is no indication that chlorination is the mechanism responsible. For a discussion of the currently accepted mechanism for PCDD formation in chlorophenol manufacturing, see the following discussion on pentachlorophenol. Other workers (e.g., Firestone et al. 1972) have analyzed technical formulations of dichlorophenolics and found no dioxin contamination.

D. Pentachlorophenol (PCP) production

Generally, the incidental formation of PCDDs during pentachlorophenol manufacturing is thought to be due to the strong basic conditions and condensation of the chlorophenolate salts with each other (see US EPA 1980 for discussion of reaction mechanism). The initial condensation forms a polychlorodiphenyl ether, which then undergoes an intra-molecular reaction to form polychloro-p-dibenzodioxin. Since technical pentachlorophenol has significant levels of tetrachlorophenols, the PCDD distribution is predominated by OCDD, followed by varying amounts of HpCDD and HxCDD. Generally, PCDFs are at much lower levels. It is also notable that polychlorohydroxydiphenyl ethers are co-contaminants of PCP (Jensen and Renberg 1972; Jensen and Renberg 1973; Nilsson et al. 1974). This fingerprint or product distribution does not resemble any product distribution associated with known sources of OCS. There is no similarity

in the reactions responsible for PCDD formation in PCP manufacturing (which are largely ionic) and the *de novo* high energy free radical chlorination and coupling reaction described by Schulman and Klingele (1985). There is no indication that any of the other OCS precursors are present. Thus, no evidence has been presented or is available indicating that there is any similarity to the mechanism for PCDD formation in pentachlorophenol and any known mechanism for OCS formation.

19

VI. Estimating an OCS Inventory Based on the Presence of PCDD/F

The Battelle report outlines a series of assumptions around ratios of HCB, PCDD/F, and OCS to develop emission factors, then uses the Oheme et al. (1989) sediment data to develop a numerical ratio for extrapolating PCDD/F data to predict or inventory other OCS sources. As was discussed previously, the fingerprint from the metals refining process studied by Oheme et al. (1989) was specifically noted by the authors to be unique. This is actually data that indicate that one should not use this as the basis of a conversion factor for any source other than other metal refining processes, or perhaps the chlor-alkali process, since it clearly demonstrates that this source is unique. Until a link has been established between OCS and a given mechanism of PCDD/F formation, it is totally inappropriate and counterproductive to the goals of the Binational Toxics Strategy to generate “generic” PCDD/F-to-OCS emission factors to estimate source emissions or to develop an OCS inventory. Thus the entire rationale used in Section 4.2 to establish a cornerstone for developing an OCS source inventory is fatally flawed and should be discarded.

20

Fate Based OCS Release Rate Estimation

Mr. Robert Bailey has reviewed the premise put forth in the second Battelle report regarding the calculation of OCS/HCB/Dioxin ratios from sediments, and their application to suspected source generation rates. He has found this presentation to be seriously flawed. Estimates of OCS releases to the Great Lakes Basin have been grossly over estimated. His comments follow.

As the Battelle authors found when attempting to compile a report on sources of octachlorostyrene (OCS), there is essentially no direct information available on production and releases of OCS. Their approach was to summarize what information they found on the occurrence of OCS in the environment and potential sources. However, there was no segregation of the data by time so that the conclusions are based in large part on older information, reflecting technology and practices from the 1970s and earlier. In addition surrogates were incorrectly used to estimate OCS emissions and concentrations in the environment. **The conclusion that OCS may be currently, 1999, emitted in significant quantity in the Great Lakes region is not supported by the available data.** The reported dramatic decreases in most of the observed concentrations over the past 30 years and concurrent and continuing decreases in related chemicals suggest that OCS may be disappearing from sight in the Great Lakes.

Environmental Concentrations

In the Great Lakes and elsewhere the observation of OCS in the environment has been the clue to production and release of OCS from a variety of industrial processes. Sediment cores in Lake Ontario show a peak in the concentration of many chlorinated chemicals, chlorobenzenes, pesticides and OCS around 1960 (Kaminsky and Hites, 1984, Durham and Oliver, 1983)¹⁶. Since that time, waste disposal as well as production technology have improved with great reductions in the release of these chemicals to the environment. In fact, already by 1981 Durham and Oliver (1983) reported the concentration of OCS in Lake Ontario sediments had dropped by over 95% from its 1960 concentration. Huestis et al. (1996) report an approximately 90% decrease in the concentrations of both OCS and HCB in fish from Lake Ontario between 1977 and 1993. The concentration of OCS in Niagara River suspended sediments has continued to drop during the period of 1990 through 1995 (Niagara River TMP).

Sources of OCS

The major recent (post-1980) sources of OCS in the environment seem to have been landfills which received waste from the old processes (pre-1980) described in the Battelle report. For example, prior to the 1970s landfill in the Niagara Falls area received “taffy tar” containing OCS and many other chlorinated organics from the production of chlorine. However the release of OCS from these old landfills has been and will continue to be reduced by (a) cleaning old storm sewers of accumulated chemicals and (b) diverting the current landfill leachate from the landfills to wastewater treatment (Niagara River TMP). This storm sewer cleaning and landfill leachate diversion to wastewater treatment has been and is an ongoing part of the cleanup of the Niagara River.

A second example of reduced OCS emissions is the cleanup of the Ashtabula River. Emissions of OCS and other chlorinated chemicals into the Ashtabula River have been essentially eliminated and a dredging program is planned to remove contaminated sediments which could spread into Lake Erie (Mahan, 1999).

The formation of trace levels of OCS has been documented for a number of processes where chlorine and carbon are present at high temperatures or in electrochemical reactions (Vogelsang, 1986; Kaminsky and Hites, 1984). In general these processes have not been studied closely for OCS because of its low concentrations. As suggested by Schulman and Klingele, it is logical to attempt to predict OCS emissions from the HCB or PCDD/Fs emissions from a variety of processes. The formation of OCS along with HCB, hexachlorobutadiene and polychlorodioxins and furans (PCDD/Fs) from the successive accumulation of two-carbon units, as proposed by Schulman and Klingele, is easy to accept based on the pyrolysis experiments of Lahaniatis (1989). Similarly, the pyrolysis of hexachloroethane used in degassing of molten aluminum in laboratory experiments by Westberg et al. (1997) and qualitatively confirmed by Vogelsang (1986) is consistent with Schulman and Klingele’s proposal. However, the formation of PCDD/Fs seems to

16 For complete description of references see bibliography contained in Appendix VIII

have a large surface catalysis component which varies widely under different conditions and may be different for OCS. The variations reported in the mixtures of PCDD/Fs from different processes also introduce a great deal of uncertainty in the ratio of OCS production to that of PCDD/Fs. (Summing the different congeners based on their toxicity to calculate a TEQ adds another layer of uncertainty). HCB is chemically more like OCS so that it may be a better surrogate for estimation of OCS concentrations in the environment. However, neither HCB nor TEQ can be considered a good surrogate for OCS in the absence of information linking OCS to each of the wide variety of processes considered in the Battelle report.

In addition, HCB is formed as a byproduct in some specific reactions in the production of highly chlorinated pesticides such as dimethyl tetrachloroterephthalate. Thus, the use of surrogates such as HCB, in the absence of specific information on emission ratios, must be used for only preliminary, order of magnitude, estimates of OCS emissions. Differences in the environmental degradation rates of OCS and surrogates could also change the observed ratio, especially in old samples, and not enough information is available at present to confidently assign the expected change in ratio.

Estimates of OCS emissions from HCB and PCDD/Fs were made in the Battelle report. However, this author will outline below several defects in the Battelle report's estimates of OCS emissions. The first error was taking the relative concentrations of OCS and HCB in sediments as reflecting their water concentrations without correcting for their different partition coefficients. Also, the Battelle report based its ratio of OCS to TEQ (PCDD/F) solely on data from a study of one river, the Elbe. This author proposes using an alternative study based on 400 sites in the U. S. (Kuehl and Butterworth, 1994).

The use of HCB concentrations in environmental samples as a measure of OCS needs to take into account their different physical properties which affect their partitioning in the environment. Neutral chemicals adsorb on sediments in proportion to their octanol/water partition coefficient, Kow (Karickhoff et. al., 1979). The log Kow of OCS is estimated to be approximately 7.46 from structure activity correlations (SRC online Kow) and the log Kow of HCB, approximately 5.5 (Mackay et. al., 1992). Thus, OCS is estimated to adsorb about 100 times more strongly on sediments than HCB. That is, the concentration of OCS on sediment would be 100 times that of HCB at equal water concentrations.

The OCS/HCB sediment concentration ratio for some sediments are:

Durham and Oliver (1983)	0.15, mean, 1900-1981, Lake Ontario
Oliver and Bourbonniere (1985)	0.11, mean, 1980, 1982, Lakes Huron, Erie
Krieg and Krausch (1993)	0.15, mean, 1985-87, Elbe Estuary
Drouilliard et al. (1996)	0.26, mean, 1996, Detroit River

Thus, the concentration of OCS is estimated to be between 0.01 and 0.001 of that of HCB in the water. Presumably, the relative concentrations of OCS and HCB originally emitted would therefore also be between 0.01 and 0.001.

Atmospheric concentration measurements of OCS and HCB are likely to represent current emission ratios. However, such measurements have not been carried out extensively. Hoff et al. (1992) reported atmospheric measurements of OCS and HCB in 1988-89 in Canada near the shore of Lake Ontario. Unfortunately due to experimental design error, their sampling system did not collect all of the HCB during the summer but still the mean concentrations of HCB were nearly 100 times those of OCS, 54 vs. 0.71 pg/m³. More recent measurements by Dan et al. (1999) did not detect OCS most of the time. HCB is included in the suite of compounds being regularly monitored in the International Atmospheric Deposition Network (IADN) program in the Great Lakes. Results from this program generally show a substantial and steady decline in atmospheric concentrations of HCB and other chlorinated chemicals since 1991 (Cortes et al., 1998, Hillery et al., 1997).

A factor for estimating the environmental concentration of OCS relative to that of 2,3,7,8-TCDD can be derived from the work of Kuehl and Butterworth (1996) in their survey of fish from nearly 400 sites throughout the United States. They report a mean concentration of 2,3,7,8-TCDD in fish of 13.6 pg/g, which made up 55% of the TEQ and a mean of 1.7 ng/g OCS. Converting the mean TCDD concentration to TEQ gives 25 pg/g TEQ which yields an OCS/TEQ ratio of 1700/25 or 68. Correcting for the increased bioaccumulation factor of OCS, 117×10^6 , vs. TCDD, 9×10^6 (Battelle report) suggests a concentration factor of $68/(9/117)$ or OCS = 5.2 TEQ. Using this procedure, the concentration of OCS in the environment, and presumably emissions, would be five times the TEQ concentration. This factor can be compared with the OCS/TEQ factor of 653 used in the Battelle report which was derived from data in the Elbe River. The large number of non-detected OCS concentrations which were included at half the detection limit in the study by Kuehl and Butterworth lead to some uncertainty in the factor of five but this uncertainty is probably less than the overall uncertainty in using such a surrogate for OCS as TEQ.

Mr. LaFleur has shown that the one-size-fits-all approach used by Battelle to suggest OCS sources is flawed. Additionally, the errors discussed above in the procedure which were used to establish their ratio factors produce erroneous release rate figures. Going through Table 4 of the Battelle report applying a multiplier of 5 to the dioxin emissions and 0.01 to the HCB emissions yields a different perspective on OCS emissions, about 60 pounds OCS emissions per year for the entire U. S. versus the 4000 pounds estimated in the Battelle report. Dr. Smith's review of OCS levels in the environment have led him to the conclusion that air deposition is not a significant input vector for the Great Lakes. Given this finding, out-of-basin sources must be discounted from the 60 pound per year figure. Once the correct analytical data is used to determine if a source or sector actually releases OCS, the proper surrogate ratio is identified and applied, the "source" is only included if it is in the Great Lakes Basin, and the continuing operation of the "source" is confirmed, the actual Great Lakes Basin OCS release numbers will be substantially lower, and probably not significant.

These findings lead to the conclusion, that neither the current analyses for OCS in the environment or emission estimates based on surrogates support the Battelle report conclusion that there are significant emissions of OCS in the Great Lakes Basin.

OCS Pollution Abatement Technologies (A pollution prevention approach)

As can be seen from the forgoing discussions, industries have used pollution prevention techniques to limit or eliminate OCS releases. In the case of the solvents industry, entire processes have been shut down. In other industries like the aluminum smelters, chemical substitutions have been made. The change from the graphite electrode process to metal electrodes in the chlor-alkali industry serves as an example of process technology changes which have resulted in the elimination of OCS sources. In other industries pollution control technologies have virtually eliminated OCS releases. Chemically assisted scrubbing equipment such as that employed by some aluminum smelters provide additional assurance that OCS and other compounds are not released in significant quantities. Utilization of these measures demonstrate that actions have been taken, over the past couple of decades, during a timeframe largely ignored by the second Battelle report which has provided for the virtual elimination of OCS releases from many industrial sources.

Findings and Conclusions

The following findings and conclusions can be drawn from the information provided above:

The Findings

This work has produced the following findings.

- In many industry sectors, pollution prevention measures have eliminated or significantly reduced OCS releases.
- In other sectors, Great Lakes Basin located processes which had previously released OCS have been shut down.
- In a few sectors, continuing OCS releases, if they actually occur at all, are at very low, often not detectable, levels.
- The examination of OCS environmental trend data shows that concentrations are decreasing rapidly. They are at or approaching detection limits in most media. If remaining OCS sources were significant, it would be expected that environmental concentration trends would be reaching a plateau, or in the worst case scenario, increasing.

The Conclusions

Based on the sector by sector analysis results and environmental trend data described in this report it is concluded that, for the sectors for which we have data, contemporary industrial sources of OCS in the Great Lakes ecosystem have been virtually eliminated¹⁷.

¹⁷ The primary focus of this study has been the Great Lakes Basin. However, also included in this report is information pertaining to the likelihood of OCS releases at St. Lawrence River watershed based (Quebec) magnesium production and copper recycling (electronic equipment) facilities. Emissions potential at both was found to be unexpected or small.

This status has been achieved through exercise of pollution prevention and pollution control measures.

Appendix I
Octachlorostyrene Work Sheet

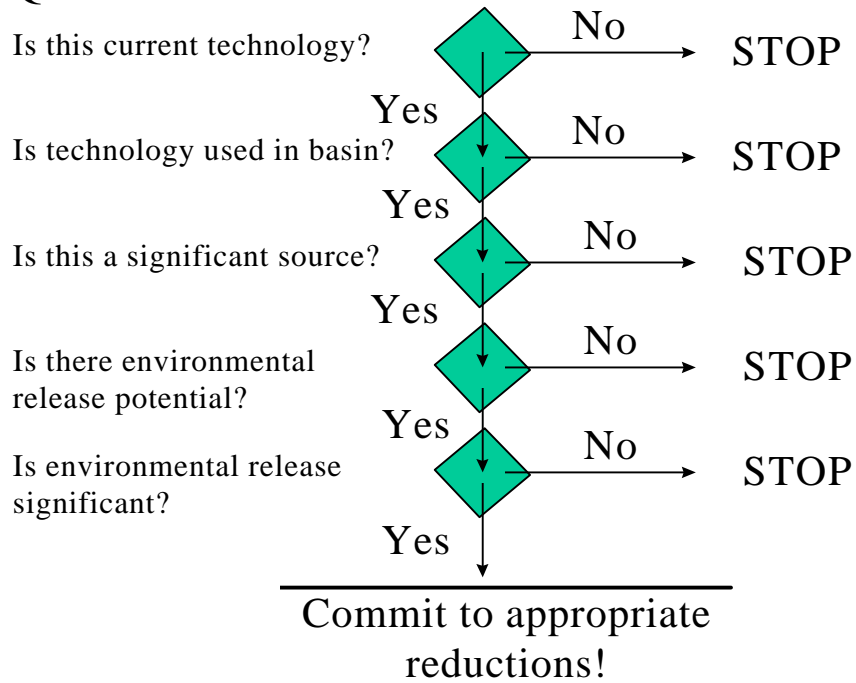
<u>Potential Sources of OCS</u>	<u>Current Technology</u>	<u>Basin Technology</u>	<u>Source Significant</u>	<u>Environmental Release Potential</u>	<u>Significant Release Potential</u>
Chlor-alkali production					
Graphitic electrodes	No	STOP			
Magnesium production					
Graphitic electrodes	Yes	No	STOP		
Raw material chlorination					
PVC Incineration					
Medical wastes					
Municipal wastes	Yes	Yes	No	Stop	
Chlorinated solvent incineration					
Cement kilns					
Haz. Waste incinerators	Yes	Yes	No	Stop Stop Stop	
Medical waste incinerators	Yes	Yes	No		
Municipal wastes incinerators	Yes	Yes	No		
Petroleum catalyst regen.					
PCB incineration					
Waste oil burning					
Auto fuel combustion	Yes	Yes	No	Stop	
Metal degreasing	Yes	Yes	N/A	No	STOP
Aluminum production					
Pri. - graphitic electrodes	Yes	Yes	No	STOP STOP	
- degassing with Cl ₂	Yes	Yes	No		
Sec. - Chlorinated coatings	No	STOP			STOP
- demagging with Cl ₂	Yes	Yes	No	STOP	

PVC coated wire recycling	Yes	Yes	No	Stop	
PVC polymerization/production	Yes	Yes	No	Stop	
Pesticides Manufacture					
Mono to tetrachlorophenol prod.	Yes	Yes	No	STOP	
Pentachlorophenol production					
Wood preservation	Yes	Yes	No	Stop	
Rare metals production					
Niobium extraction					
Tantalum extraction					
Pulp and Paper Making					
Chlorine bleaching	No	STOP			
Chlorinated solvent production					
High temp. chlorination	Yes	Yes	No	STOP	
Coke production	Yes	Yes	No	STOP	
Waste Sites					
Graphitic electrode disposal	N/A				
Electrolysis sludge disposal	N/A				
Incineration ash disposal	N/A				
Landfill fires	N/A				
Tire manufacturing	Yes	Yes	No	STOP	
dkp/3-8-98					

Appendix II

OCS Decision Tree

Questions:



Appendix III

Figures 1 - 12

Status and Trends of OCS In Great Lakes Media

Figure 1. First order decline (10% per year decrease) on linear XY plot

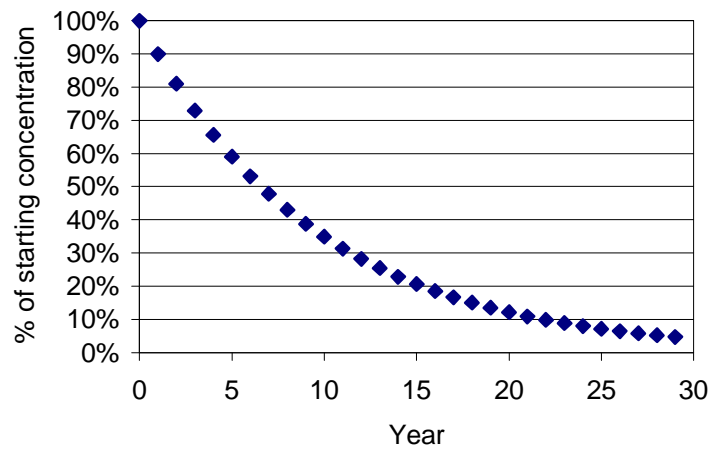


Figure 1. A first order decline graphed on the more usual linear XY plot.

Figure 2. First order decline (10% per year decrease) on semi-log XY plot

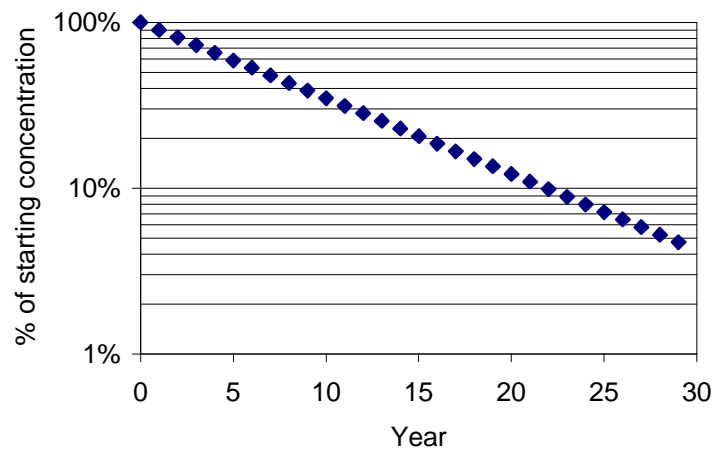


Figure 2. The same first order decline plotted on semi-log paper.

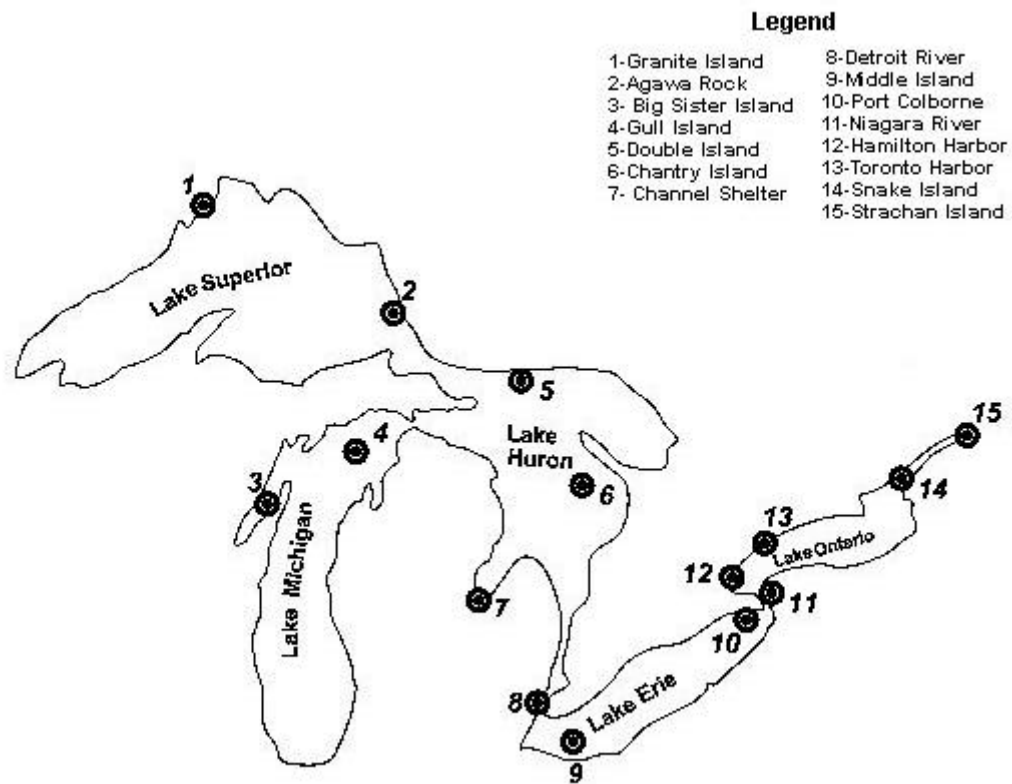


Figure 3. Location of Herring Gull colonies on the Great Lakes.

Figure 4. Yearly % Decline vs. Colony

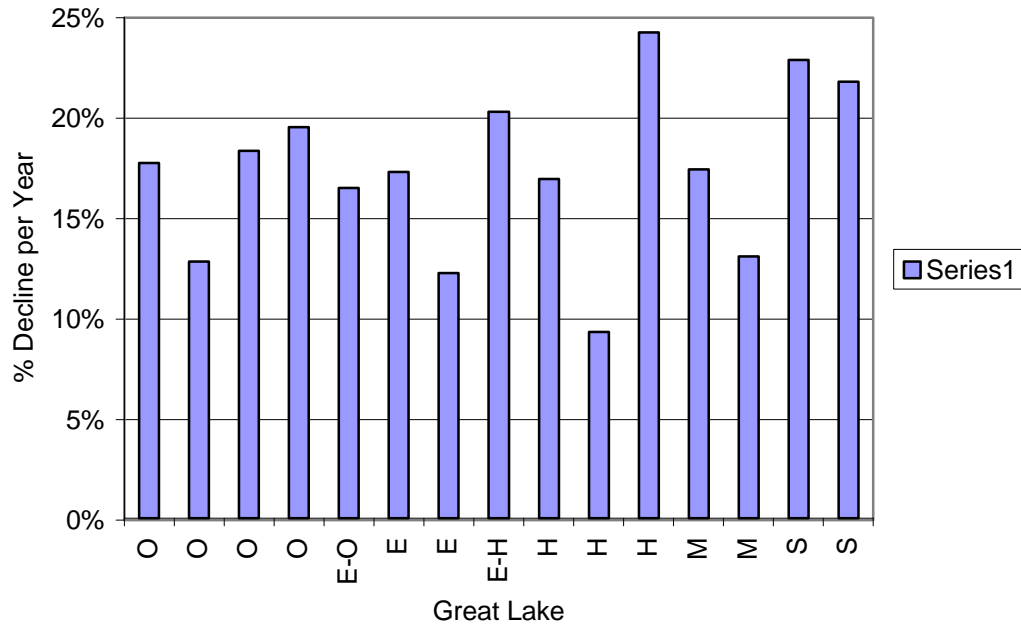


Figure 4. Best-fit % declines per year estimated from linear regression. Colonies are plotted in the following order which generally follow an east-west gradient: Lake Ontario colonies in the order of Strachan Island, Snake Island, Leslie Spit, Hamilton Harbor, Niagara River, Lake Erie colonies in the order of Port Colborne and Middle Island, Detroit River, Lake Huron colonies in the order of Channel Shelter Island, Chantry Island, and Double Island, Lake Michigan colonies with ?/ and ??, and Lake Superior colonies Agawa Rock and Granite Island.

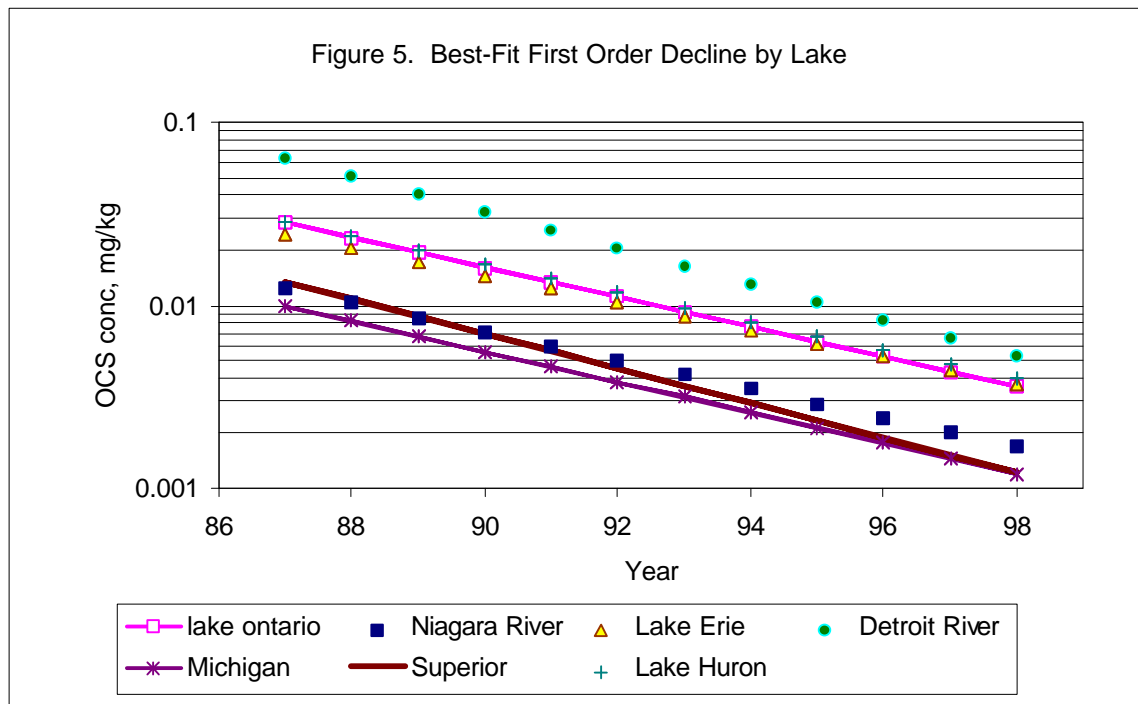


Figure 5. Best-fit declines of OCS in herring gull eggs grouped by Lake and Connecting Channel.

Figure 6. Mean OCS (94-98) versus Lake

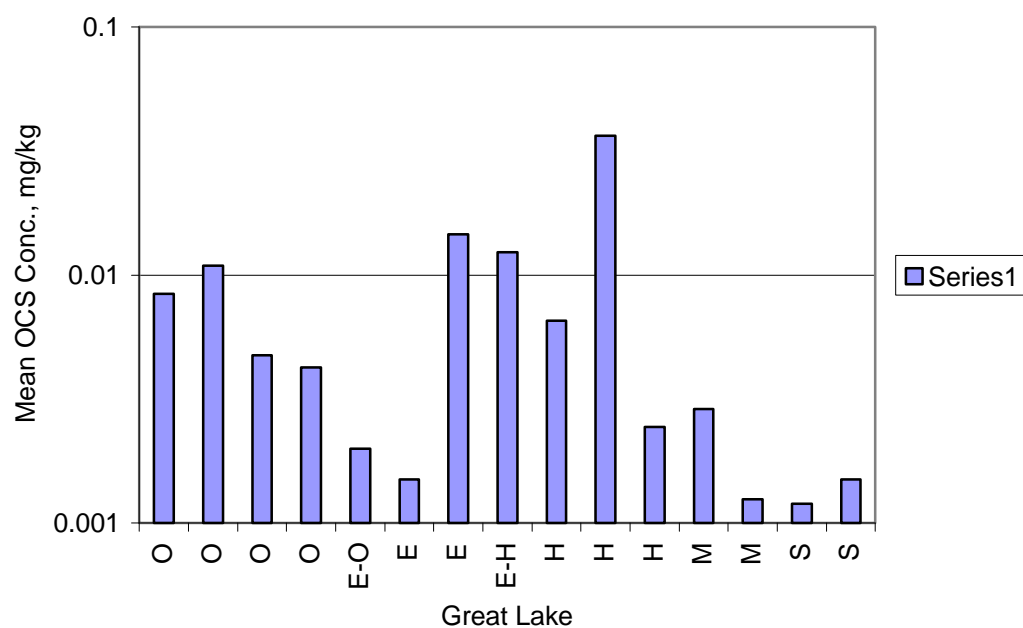


Figure 6. Most-recent (1994 to 1998) concentrations of OCS by colony. Sequence of colonies same as in Figure 6.

Figure 7. OCS in Spottail Shiners in Lower Niagara River (MOE Data)

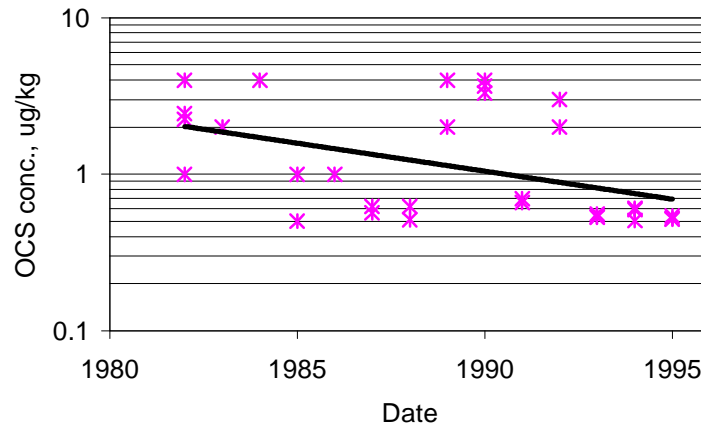


Figure 7. OCS concentrations in spottail shiners from the lower Niagara River. Values less than detection limit (1 ug/kg) set equal to 0.5 ug/kg. Some data points have been altered somewhat (e.g., 10% to 20%) to aid viewing when more than one sample on the same date had the same concentration.

Figure 8. Estimated whole water concentrations of OCS at
Niagara-on-the-Lake

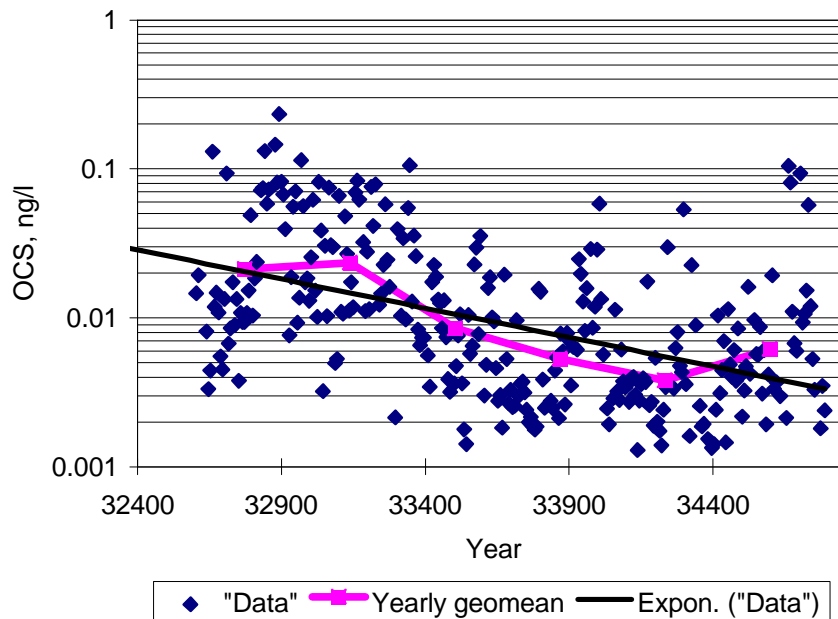


Figure 8. Concentrations of OCS in Niagara River water at the mouth of the Niagara River.

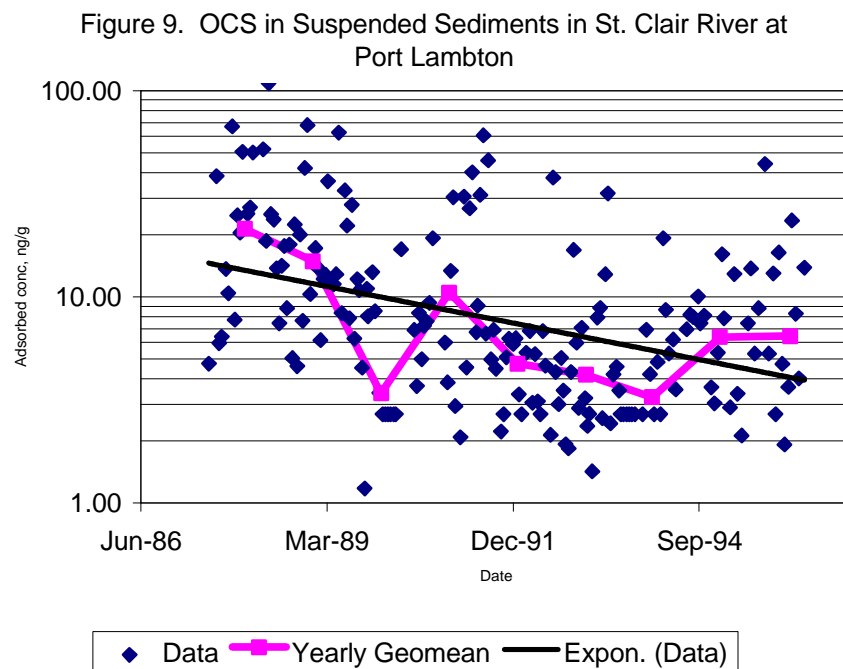


Figure 9. Concentrations of OCS on suspended particle from the St. Clair River at Port Lambton.

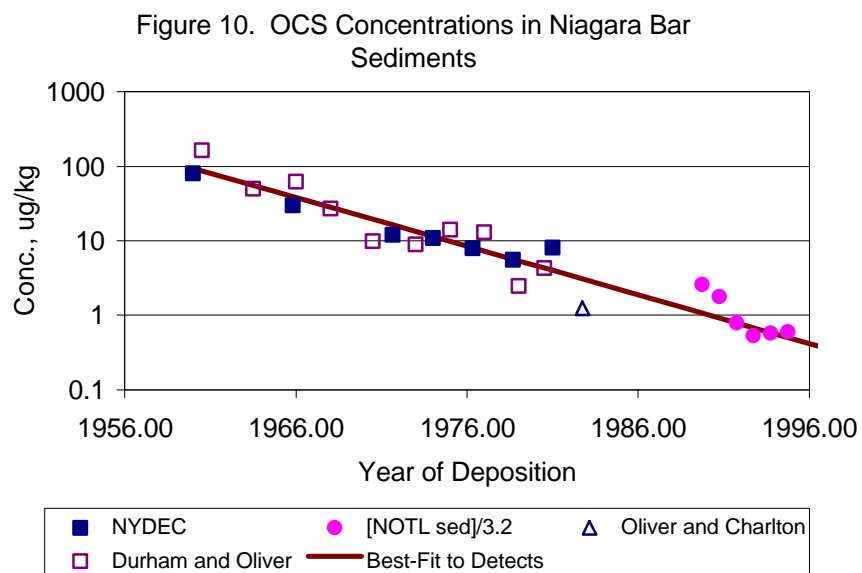


Figure 10. Concentrations of OCS in sediments from Lake Ontario. For the NYDEC sample, all analyses for sediments deposited between 1981 and 1995 were below the detection limit, but these data are not depicted on this graph.

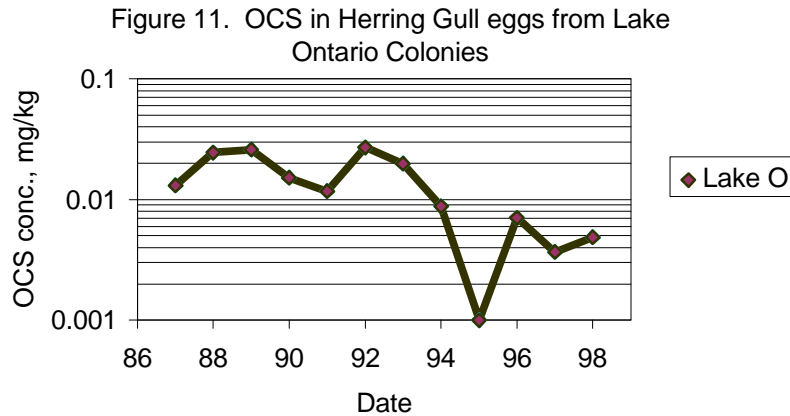


Figure 11. Mean concentrations of OCS in gull eggs from the four Lake Ontario gull egg colonies (Strachan Island, Snake Island, Leslie Spit, and Hamilton Harbor.)

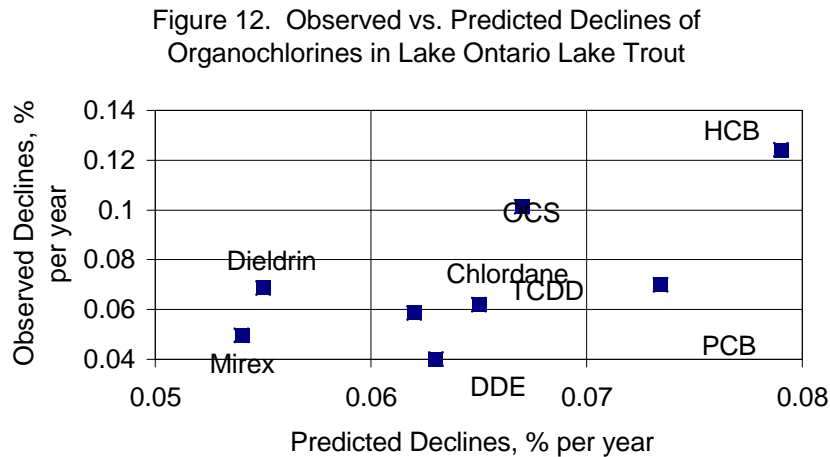


Figure 12. Observed versus predicted declines of different organochlorines in Lake Ontario lake trout. Predicted rates of decline (per year) from the Endicott et al. model (1992a) after cessation of loading. Observed rates are best-fit declines observed in lake trout, data from Huestis et al. (1996).

Appendix IV

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Status and Trends of OCS in Great Lakes Media

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Appendix V

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